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Recent Advances in Poly(pyrazolyl)borate (Scorpionate) Chemistry

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I. Introduction

Since their introduction in 1967, poly(pyrazolyl)-borates[1] have found wide application in coordination chemistry, and their complexes with most metals or metalloids of the periodic table have been prepared. The growth of this area accelerated since the introduction of the coordination-controlling "second generation" ligands[2] in 1986, none of which were mentioned in the most recent reviews which were devoted only in part to poly(pyrazolyl)borates.[3] These reviews included the literature through much of 1984; the present review covers the time from 1984 to early 1993, along with a few earlier references, which were previously missed. We are excluding the neutral heterocycles pyrazaboles, R$_2$B(pz*)$_2$BR$_2$, which may be formally regarded as boronium poly(pyrazolyl)borates, and we also exclude poly(pyrazolyl)methanes which are neutral analogs of poly(pyrazolyl)borates and which exhibit very similar coordination chemistry. The subject matter is divided into two main categories: (1) the chemistry of novel poly(pyrazolyl)borate ligands, reported since the last review, organized by ligand type, and (2) the chemistry of previously reported ligands, subdivided into bidentate and tridentate (mostly HB(pz)$_3$ and HB(3,5Me$_2$pz)$_3$), the latter being organized by periodic table groups.

Throughout the years, poly(pyrazolyl)borates have been compared to β-diketonates, when bidentate [R$_2$B(pz)$_2$ = 1], or to Cp, Cp*, when tridentate [RB(pz)$_3$ = 2], as shown:[4]

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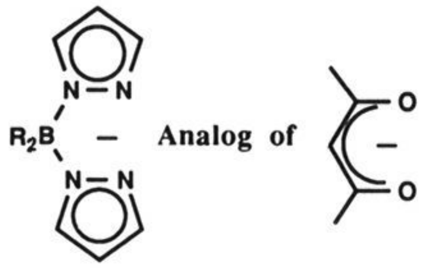
Swiatoslaw Trofimenko was born in Lviv, Ukraine, and received his B.A. degree at Wesleyan University in 1955. He received his Ph.D. degree in 1958 with Professor Charles D. Hurd in organic chemistry at Northwestern University. After one year of post-doctoral research with Professor G. Stork at Columbia University, he joined the Du Pont Central Research Department in 1959. His research there encompassed cyanocarbons, polyhedral boranes, polyformyl compounds, diazapentalenes, cyclometalation (a term which he coined), boron and pyrazole chemistry, including polypyrazolylborates, a ligand class which he discovered and extensively developed. In 1973 he spent one semester as the Richard Merton Visiting Professor at the University of Münster, Germany. From 1977 to 1980 he was Manager of the Du Pont office in Warsaw, Poland. Thereafter, he returned to the United States and has continued research in the areas of catalysis, fluorine chemistry, as well as in polyamide and polyimide chemistry, at various divisions of the Du Pont Company. A member of the American Chemical Society, he has held offices at the regional and national level.



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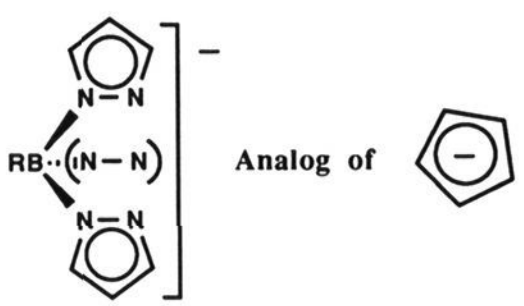

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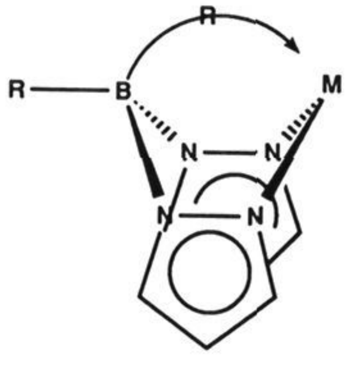
While such comparisons had some value in describing poly(pyrazolyl)borates in terms of known ligands, they were not helpful at all in underscoring the unusual and specific features of this ligand class. In particular, such comparisons failed to provide an understanding of the close relationship of the bis- and tris(pyrazolyl)borates, and the presence of a continuum in their coordinative behavior. Thus, it has become necessary to come up with a superior analogy which would treat this whole ligand class in a comprehensive fashion and which would help in understanding the key features involved.

Table I. Comparison of C_5R_5 (= Cp^R) and $RB(3R,4R,5R\text{-pz})_3$ (= Tp^R) Ligands

	Cp^R	Tp^R
Common Features		
electrons donated	6	6
coordination sites occupied	3	3
charge	−1	−1
Differentiating Features		
symmetry of LM Fragment	C_{5v}	C_{3v}
substitutable positions	5	10
number of possible R-substituted ligands *with retention of the original symmetry* (*isosymmetric*)	1	4 (mono) 6 (bis) 4 (tris) 1 (tetrakis) 15 total
monomeric LMX available? (X = halide)	no, (except for Be)	yes
uncharged isosteric, isosymmetric, and isoelectronic analog?	no	yes, known (C-based)
−2 charge, isoelectronic, and isosymmetric analog?	no	yes, unknown (Be-based)

The fundamental feature in all poly(pyrazolyl)borate complexes is the six-membered ring $RR'B(\mu\text{-pz*})_2M$ (where M may contain additional ligands), and where R, R′ can be H, alkyl, aryl, NR_2, ArS, or pz* (pz* = 1-pyrazolyl or substituted 1-pyrazolyl). Because of the bond angles and distances involved, this ring has almost always a boat structure of varying depth. In such a structure (3), the pseudoaxial group R is curled toward the metal and may bond to it, interact with it, or just screen it.



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Nature provides the closest analogy encompassing these features in the scorpion. This creature grabs its prey with two identical claws [= $(pz^*)_2$] and then may proceed to sting it with the sharp point of the curving tail (= pseudoaxial R). Therefore, I found it appropriate to coin the term "scorpionate ligands" to describe the poly(pyrazolyl)borates, and the versatility of their coordination chemistry becomes explainable in terms of variations on the sting theme.

Two types of scorpionate ligands may be distinguished:

The first is "homoscorpionates" (1), where the pseudoaxial R group is pz* (i.e. the sting becomes a third claw, identical to the other two) and the ligand is of local C_{3v} symmetry. These are the most commonly used ligands. Their key similarities and dissimilarities, as compared with the Cp family, are tabulated in Table I.

It should be noted that the number of possible variants (15) for the ligand $RB(3R,4R,5Rpz)_3$ in Table I applies to cases where R is either H, an alkyl, or aryl group (all non-hydrogen substituents being the same). When the non-hydrogen substituents are nonidentical, the number of variants is greatly increased.

The second type is "heteroscorpionates" (2), where the coordinating pseudoaxial R is anything but pz*; it can, however, be a differently substituted pz group. In addition, the R bridge may be monoatomic or diatomic.

Known examples of a monoatomic "sting" are H, SAr, NMe_2; diatomic "stings" include pz (when different from pz*) and -CH groups, forming agostic bonds to the metal. One type of pseudoaxial group which never functions as a sting is a phenyl group in $Ph_2B(pz)_2$ complexes.

Although one would have thought that the wealth of controllable variables, available for choosing the sting in heteroscorpionates, would make this type of ligand widely studied, this has not been the case. In the 1984–1993 period only about 5% of the over 400 poly(pyrazolyl)borate publications dealt with heteroscorpionate ligands, the rest with homoscorpionates. Clearly, there is an untapped potential in heteroscorpionates to be exploited.

A. Abbreviations

Throughout the years, coordination chemists have worked predominantly with two poly(pyrazolyl)borate ligands: $HB(pz)_3$ and $HB(3,5Me_2pz)_3$. Curtis[5] introduced the abbreviation Tp for the former and Tp* for the latter. However, this is not enough, since there has been a rapid development of other homoscorpionate ligands containing diverse substituents, mainly at the 3 position, but also at the 5- and 4-positions. These affect the accessibility of other ligands to the metal in L*M moieties, and other aspects of L*M coordination chemistry, raising the issue of finding additional ways of compactly denoting these new ligands.

For the sake of convenience we are adopting the Tp nomenclature, with Tp and Tp* denoting $HB(pz)_3$ and $HB(3,5Me_2pz)_3$, respectively. The ligand $B(pz)_4$ will be represented by pzTp. Other homoscorpionate ligands are identified on the basis on the Tp abbreviation, aiming at the most streamlined way of representation, and using the following conventions:

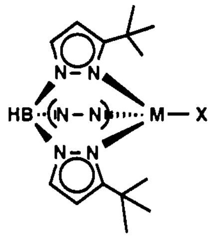
1. The 3-substituent is denoted by a superscript over Tp; thus Tp^{iPr} is $HB(3\text{-}Pr^ipz)_3$, Tp^{tBu} is $HB(3\text{-}Bu^tpz)_3$, Tp^{Ph} is $HB(3\text{-phenylpz})_3$, etc. This is because 3(5)-monosubstituted pyrazoles invariably bond to B with the substituent ending up in the unhindered 3-position.
2. The 5-substituent, except for H, follows the 3-substituent, separated by a comma; thus, $Tp^{iPr,Me}$ is $HB(3\text{-}Pr^i\text{-}5\text{-}Mepz)_3$. When the 3- and 5-substituents are identical, the 3-R group is followed by a 2; thus Tp^{Ph2} is $HB(3,5\text{-}Ph_2pz)_3$, etc.
3. The 4-substituent is denoted by a superscript 4R; thus, Tp^{iPr4Br} is $HB(3\text{-}Pr^i\text{-}4\text{-}Brpz)_3$, and Tp^{4Me} would be $HB(4\text{-}Mepz)_3$, etc.
4. No abbreviations are used for heteroscorpionates.

II. Novel Scorpionates

A. Homoscorpionates

1. Hydrotris(3-tert-butylpyrazol-1-yl)borate [= *$HB(3\text{-}Bu^t\text{-}pz)_3$ = Tp^{tBu}*]

The ligand Tp^{tBu}, prepared from 3-*tert*-butylpyrazole and KBH_4 ($H_2B(3Bu^tPz)_2K$ and $B(3Bu^tpz)_4K$ were prepared similarly), was the first of the "second generation" scorpionate ligands. Its coordinative behavior reflected the severe screening of the metal in the $Tp^{tBu}M$ fragment, so that with first row transition metals (Mn to Zn) only four-coordinate tetrahedral complexes of type $Tp^{tBu}MX$ (4) were obtained (X = Cl, NCS, NCO, N_3), which resisted solvation. The cone angles of Tp, Tp*, and Tp^{tBu} are 184°, 224°, and 244°, respectively. No $(Tp^{tBu})_2M$ species could be obtained, in contrast to Tp and Tp*.[6] The structure of $Tp^{tBu}Tl$ was established by X-ray crystallography; it is of local C_{3v} symmetry (disregarding the rotameric disposition of the *tert*-butyl groups), with the Tl atom bonded equally to the three coordinating nitrogen atoms.[7] The reaction of $Tp^{tBu}MCl$ with $AgBF_4$ results in formation of $Tp^{tBu}MF$.[8]



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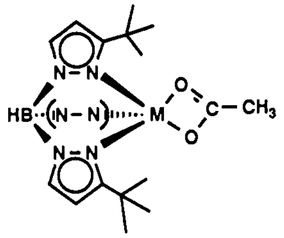

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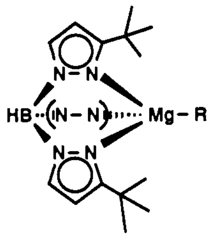
Five-coordinate complexes (5) could be obtained with chelating bidentate ligands of low steric hindrance. The ligand Tp^{tBu} gave rise to several new and unique types of complexes. Thus, reaction of $Tp^{tBu}Tl$ with MgR_2 (R = Me, Et) provided the first example of stable monomeric, unsolvated alkylmagnesium compounds $Tp^{tBu}MgR$ (6), and the MgMe derivative was characterized by X-ray crystallography.[9] $Tp^{tBu}MgR$ derivatives with R = iPr and tBu were prepared similarly and were found to react with oxygen, forming alkylperoxo compounds $Tp^{tBu}Mg\text{-}OO\text{-}R$. These transfer one oxygen atom to PPh_3 and are converted to alkoxo derivatives, $Tp^{tBu}Mg\text{-}OR$.[10] However, the reaction of $Tp^{tBu}MgCH_2SiMe_3$ with oxygen produced $Tp^{tBu}MgOSiMe_3$, as a result of facile cleavage of the Si–C bond.[11] A study of the reaction of $Tp^{tBu}Tl$ with various RMgX reagents showed that metathesis of the Mg-R bond is favored for X = Cl or Br, but that metathesis of the Mg-X bond dominates when X = I.[12]

In a more detailed synthetic and structural study additional $Tp^{tBu}MgR$ complexes were prepared (R = $CH{=}CH_2$, Ph, CH_2SiMe_3), the structures of several of which ($Tp^{tBu}MgMe$, $Tp^{tBu}MgiPr$, $Tp^{tBu}MgCH_2SiMe_3$) were determined by X-ray crystallography. The synthesis of these complexes via Grignard reagents was investigated in detail, and it was found that product distribution depends on both the RMgX and the cation of the Tp^{tBu} ligand.[13] Compounds $Tp^{tBu}MgR$ are useful precursors for a variety of other tetrahedral $Tp^{tBu}MgX$ derivatives (X = SH, SMe, OEt, OPr^i, OBu^t, Cl, Br, I, NHPh, NCO, NCS, and phenyl- or (trimethylsilyl)-acetylido) mostly via reaction with the appropriate active hydrogen compounds, with concomitant evolution of RH. Surprisingly, with methyl ketones, the products are enolate derivatives, $Tp^{tBu}MgOCR{=}CH_2$.[14]

The dimethylaluminum derivative, $Tp^{Bu}AlMe_2$, was formed by the reaction of $Tp^{tBu}Tl$ with $AlMe_3$; from NMR data it has been assigned a four-coordinate structure 7.[15]

Metathesis of $Tp^{tBu}Tl$ with ZnH_2 produced the monomeric $Tp^{tBu}ZnH$, the structure of which was established by X-ray crystallography.[16] It reacts with active hydrogen compounds HX, producing hydrogen and $Tp^{tBu}ZnX$ (X = SH, $OSiMe_3$, MeCOO, phenylacetylido); with CO_2, the formate derivative, $Tp^{tBu}ZnOOCH$, was obtained, while reaction with various halides, RX, produced $Tp^{tBu}ZnX$.



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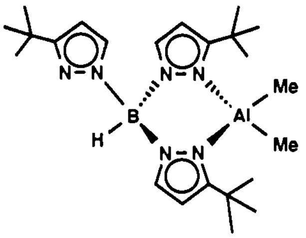

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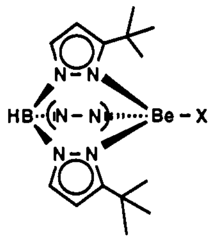
The monomeric alkylzinc derivatives, $\mathrm{Tp^{tBu}ZnR}$ (R = Me, Et), were prepared by metathesis of $\mathrm{Tp^{tBu}Tl}$ with $\mathrm{ZnR_2}$, and they exhibited reactivity comparable to that of their $\mathrm{Tp^{tBu}MgR}$ analogs.[17]

In a study of crystallographic disorder using $\mathrm{Tp^{tBu}ZnCN}$ doped with small quantities of $\mathrm{Tp^{tBu}ZnX}$ (X = Cl, Br, I), it was shown that for X = I the disorder was evident, and the individual groups could be refined, although the bond lengths were incorrect as compared with pure structures. With X = Cl or Br the disorder was not resolved.[18] Complexes $\mathrm{Tp^{tBu}ZnCl}$, $\mathrm{Tp^{tBu}ZnI}$, and $\mathrm{Tp^{tBu}ZnMe}$ were used to study changes of apparent bond lengths in single crystals, consisting of solid solutions of pairs of these compounds. The relationship between composition and apparent bond length was nonlinear.[19]

The first [tris(pyrazolyl)borato]beryllium derivatives, $\mathrm{Tp^{tBu}BeR}$ (R = Cl, Br, I, H, SH) were synthesized. Of these, $\mathrm{Tp^{tBu}BeBr}$ and $\mathrm{Tp^{tBu}BeH}$ (**8**), obtained from $\mathrm{Tp^{tBu}BeBr}$ and $\mathrm{LiAlH_4}$, were structurally characterized by X-ray crystallography. $\mathrm{Tp^{tBu}BeH}$ reacts with $\mathrm{H_2S}$, or with sulfur, yielding $\mathrm{Tp^{tBu}BeSH}$.[20]



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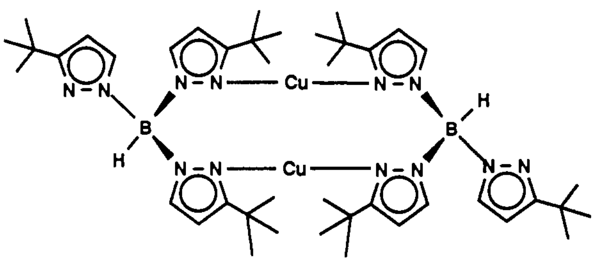
Searching for a model of nitrate reductase, the five-coordinate complex $\mathrm{Tp^{tBu}CuNO_2}$ was prepared and found to contain a bidentate nitrite ligand; it was converted to the tetrahedral $\mathrm{Tp^{tBu}CuOSO_2CF_3}$. The structures of both complexes were established by X-ray crystallography.[21] $\mathrm{Tp^{tBu}Tl}$ reacts with CuCl forming a complex **9**, isolated as the ether solvate, which contains linear N–Cu–N bonds and contains 2-coordinate Cu. This compound reacts with other ligands (MeCN, CO, NO), forming tetrahedral $\mathrm{Tp^{tBu}CuX}$ species. Of these, $\mathrm{Tp^{tBu}CuNO}$ is the first example of a mononuclear CuNO complex.[22] Structures of the tetrahedral $\mathrm{Tp^{tBu}CuCl}$ and $\mathrm{Tp^{tBu}CdI}$ have also been determined.[28]

Reaction of $\mathrm{Tp^{tBu}Tl}$ with HCl and $\mathrm{AlCl_3}$ yielded the structurally characterized $\mathrm{[Tp^{tBu}H_3Cl][AlCl_4]}$, containing a tris-protonated ligand, in which each N-bonded proton is coordinated to the chloride ion.[23] The complex $\mathrm{[Tp^{tBu}W(CO)_3]^-}$ was prepared by the reaction of $\mathrm{Tp^{tBu}K}$ with $\mathrm{(EtCN)_3W(CO)_3}$, as no reaction of $\mathrm{Tp^{tBu}K}$ with $\mathrm{W(CO)_6}$ took place. Although the NMR of $\mathrm{[Tp^{tBu}W(CO)_3]^-}$ showed a 2:1 pattern of pyrazolyl groups,[24] suggesting a possible rearrangement of $\mathrm{Tp^{tBu}}$ to $\mathrm{[HB(3Bu^tpz)_2(5Bu^tpz)]^-}$, the X-ray structure was that of pure $\mathrm{[Tp^{tBu}W(CO)_3]^-}$.[25]



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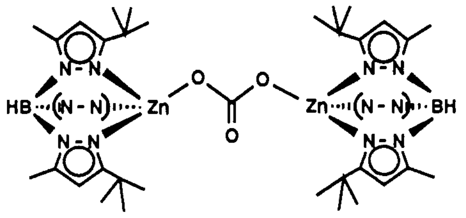
An unusual complex containing $\mathrm{Tp^{tBu}}$ functioning as a monodentate ligand, *trans*-$\mathrm{Tp^{tBu}Ni(C_6H_4}$-*p*-Me-$\mathrm{)(PMe_3)_2}$, was prepared from $\mathrm{Tp^{tBu}Tl}$ and *trans*-Ni-$\mathrm{(C_6H_4}$-*p*-Me)$\mathrm{(PMe_3)_2}$, and its structure was determined by X-ray crystallography. Complexes of *trans*-$\mathrm{Tp^{tBu}Ni[(CO)C_6H_4}$-*p*-Me]$\mathrm{(PMe_3)_2}$ were prepared similarly.[26]

2. Hydrotris(3-tert-butyl-5-methylpyrazol-1-yl)borate [= HB(3-Bu^t-5-Mepz)$_3$ = Tp^{tBu,Me}]

This ligand was prepared from 3-*tert*-butyl-5-methylpyrazole and $\mathrm{KBH_4}$ in the usual fashion. It is very similar to $\mathrm{Tp^{tBu}}$, but the presence of the 5-methyl groups offers steric protection to the B–H bond; moreover, the nonbonding repulsions of the three 5-Me groups are likely to somewhat tighten the bite of the ligand at the metal end. The fact is that $\mathrm{Tp^{tBu,Me}MX}$ derivatives show greater stability than their $\mathrm{Tp^{tBu}}$ analogs. Also, the $\mathrm{^{13}C}$-$\mathrm{^{205}Tl}$ coupling to the *tert*-butyl methyl carbons is significantly larger in $\mathrm{Tp^{tBu,Me}Tl}$ (197 Hz)[25] than in $\mathrm{Tp^{tBu}Tl}$ (171 Hz),[7] suggesting greater proximity of Tl to those carbons. The structure of $\mathrm{Tp^{tBu,Me}NiNCS}$ was determined by X-ray crystallography.[27] The complex $\mathrm{[Tp^{tBu,Me}Cu]_2}$ has a dimeric structure, similar to that of $\mathrm{[Tp^{tBu}Cu]_2}$ (**9**), while the structure of $\mathrm{Tp^{tBu,Me}CuCl}$ is different from that of $\mathrm{Tp^{tBu}CuCl}$. Also characterized by X-ray crystallography were tetrahedral complexes $\mathrm{Tp^{tBu,Me}HgI}$, $\mathrm{Tp^{tBu,Me}CdMe}$, and the five-coordinate $\mathrm{Tp^{tBu,Me}Cd(NO_3)}$.[28]

The structurally characterized $\mathrm{Tp^{tBu,Me}ZnOH}$ complex was found to act as an analog of enzyme carbonic anhydrase, in reversibly absorbing $\mathrm{CO_2}$ to yield the isolable bicarbonate complex, which reacts further forming the carbonate complex **10**.[29] The structure of this complex, and of $\mathrm{Tp^{tBu,Me}ZnO(CO)OMe}$ was determined by X-ray crystallography.[30]



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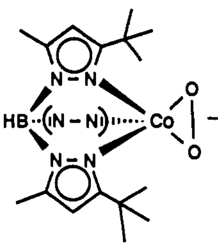
When $\mathrm{Tp^{tBu,Me}CoCl}$ was reduced with Mg in a nitrogen atmosphere, the complex $\mathrm{Tp^{tBu,Me}CoN_2}$ was obtained, which reacted with oxygen forming the superoxo complex **11**, the structure of which was established by X-ray crystallography (O–O distance 1.262 Å). It reacts with 1 equiv of $\mathrm{Tp^{tBu,Me}CoN_2}$ yielding **12**, which is also obtained from the reaction of $\mathrm{Tp^{tBu,Me}CoN_2}$ with water. Evidence of hydrogen abstraction from the *tert*-butyl groups suggested presence of a $Tp^{tBu,Me}Co\text{-}O^{\bullet}$ radical.[31]



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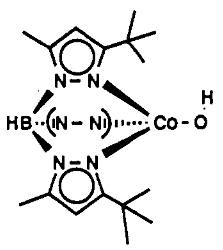

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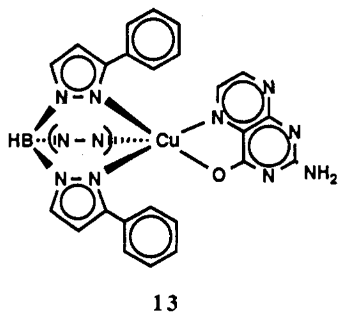
3. *Hydrotris(3-phenylpyrazol-1-yl)borate [= $HB(3Phpz)_3$ = Tp^{Ph}]*

The ligand Tp^{Ph} was one of the first "second generation" homoscorpionate ligands.[6] In contrast to Tp^{tBu}, it readily forms five-coordinate solvated species (which retain solvent tenaciously), such as $Tp^{Ph}CoNCS(THF)$, the structure of which was determined by X-ray crystallography. It takes prolonged heating in vacuo to remove the coordinated solvent, except for $Tp^{Ph}ZnX$ complexes, which precipitate unsolvated. The structures of $Tp^{Ph}ZnX$ (X = NO_3, Me, SEt) were determined by X-ray crystallography; the NO_3 ligand is asymmetrically bidentate, with one long O-Zn bond, so that Zn is five-coordinate.[32]

In contrast to Tp^{tBu}, Tp^{Ph} is capable of forming octahedral complexes, such as $Tp^{Ph}{}_2M$ (M = Fe, Mn) in the absence of strongly coordinating anions. The structure of $Tp^{Ph}{}_2Fe$ contains markedly longer N-Fe bonds than those in Tp_2Fe or $Tp^*{}_2Fe$. Also, the Fe^{III}–Fe^{II} reduction potential for $Tp^{Ph}{}_2Fe$ is about 0.6 V more positive than for Tp_2Fe.[33]

The Tp^{Ph} ligand was used in the preparation of the structurally characterized, mixed Cu-pterin complex 13[34] and of the tungsten carbyne complex 14.[35] The anion $[Tp^{Ph}W(CO)_3]^-$ was prepared directly from $Tp^{Ph}K$ and $W(CO)_6$ (in contrast to the Tp^{tBu} ligand which does not undergo this reaction), and it was protonated on W to $[Tp^{Ph}W(CO)_3]H$, the NMR of which showed the W-H bond at −2.3 ppm (J $^{183}W\text{-}^1H$ = 4 Hz).[24]



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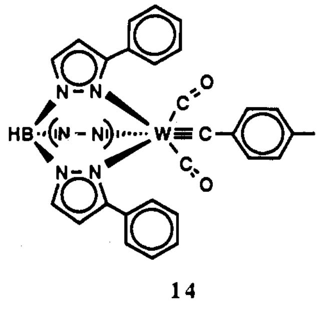

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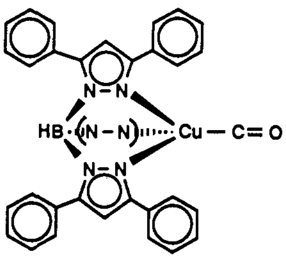
Complexes $Tp^{Ph}{}_2Sm$ and $Tp^{Ph}{}_2Yb$ were studied by NMR, and the octahedral $Tp^{Ph}{}_2Yb$, of D_{3d} geometry, was structurally characterized by X-ray crystallography.[36]

4. *Hydrotris(3,5-diphenylpyrazol-1-yl)borate [= $HB(3,5\text{-}Ph_2pz)_3$ = Tp^{Ph2}]*

The ligand Tp^{Ph2} was prepared from 3,5-diphenylpyrazole and KBH_4 in standard fashion, and it was converted to the $Tp^{Ph2}CuCO$ complex 15 which reacted with PMe_3 but not with PPh_3, to yield the $Tp^{Ph2}CuPR_3$ derivative.[37]



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5. *Hydrotris[3-(p-tolyl)pyrazol-1-yl]borate [= HB-[3(p-tolyl)pz]$_3$ = Tp^{pTol}]*

The ligand Tp^{pTol} was prepared just like Tp^{Ph}. It was characterized as the Tl salt and was converted to a variety of tetrahedral $Tp^{pTol}MX$ complexes (M = Co, Ni, Zn; X = NCS, NCO, N_3), the ligand-field spectra of which were studied.[27] The structure of $Tp^{pTol}Tl$ was determined by X-ray crystallography.[38]

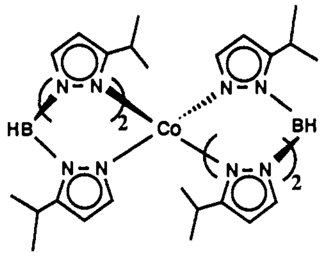
6. *Hydrotris[3-(p-anisyl)pyrazol-1-yl]borate [= HB[3(p-anisyl)pz]$_3$ = Tp^{pAn}]*

The ligand Tp^{pAn} was prepared just like Tp^{Ph}. It was characterized as the Tl salt, and was converted to a variety of tetrahedral $Tp^{An}MX$ complexes (M = Co, Ni, Zn; X = NCS, NCO, N_3), the ligand-field spectra of which were studied.[27]

7. *Hydrotris(3-isopropylpyrazol-1-yl)borate [= $HB(3\text{-}Pr^i\text{-}pz)_3$ = Tp^{iPr}] and Hydrotris(3-isopropyl-4-bromopyrazol-1-yl)borate [= $HB(3\text{-}Pr^i\text{-}4Brpz)_3$ = $Tp^{iPr,4Br}$]*

The ligands Tp^{iPr} and $Tp^{iPr,4Br}$ were prepared in standard fashion. The steric requirements of the 3-isopropyl group are intermediate between those of 3-*tert*-butyl and 3-phenyl. The effect of the 4-bromo substituent makes the $Tp^{iPr,4Br}$ derivatives more crystalline. Both ligands, Tp^{iPr} and $Tp^{iPr,4Br}$, yield tetrahedral derivatives $Tp^{iPr}MX$ and $Tp^{iPr,4Br}MX$, which form five-coordinate solvates with unhindered solvents (e.g. with MeOH but not with iPrOH), which are unstable and slowly lose solvent, reverting to the tetrahedral complexes.[39] Both regiospecifically pure ligands form octahedral $L^*{}_2M$ complexes, but this occurs with rearrangement of each ligand to $HB[(3\text{-}Pr^ipz)_2(5\text{-}Pr^ipz)]$ and $HB[(3\text{-}Pr^i\text{-}4\text{-}Brpz)_2(5\text{-}Pr^i\text{-}4\text{-}Brpz)]$, respectively, as was proven by NMR studies of the paramagnetic Co(II) complexes, and by X-ray crystallography. Formation of the rearranged complexes, such as 16, is ascribed to the molecule's inability of accommodating six isopropyl groups in the equatorial belt.

The drive toward octahedral coordination can only be effected through a 1,2-borotropic rearrangement of one pz* group per ligand.



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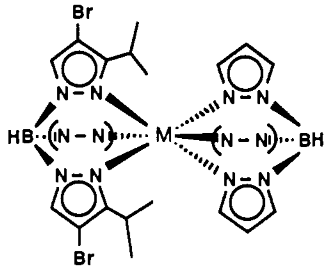
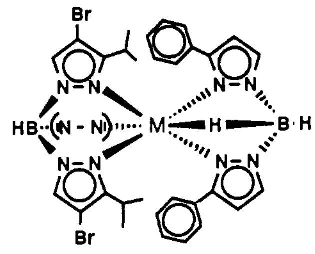


17

The structure of Tp^{iPr,4Br}CoCl was determined by X-ray crystallography.[40] In this molecule, as in other Tp^{iPr}MX or Tp^{iPr,4Br}MX complexes, the isopropyl groups are rotated so that both methyls point toward the metal. Conversely, in octahedral complexes these methyls point away from the metal, straddling in each case the pz plane. The stable Tp^{iPr,4Br}MCl complexes are very suitable for the preparation of heteroleptic compounds, Tp^{iPr,4Br}ML via reaction with L$^-$ ligands.[41] These mixed complexes were five-coordinate (L = AcAc, tropolonate, dithiocarbamate, etc.) or six-coordinate (L = scorpionate), depending on the denticity of L. When L was Tp[41] or Tp*,[42] the heteroleptic complexes were octahedral of C_{3v} symmetry, as in 17; when L was a heteroscorpionate, such as $H_2B(pz)_2$, $H_2B(3,5Me_2pz)_2$, or $H_2B(3\text{-}Phpz)_2$, the complexes were octahedral, containing one agostic B–H–M bond, as in 18. Surprisingly, the reaction of Tp^{iPr,4Br}MCl with Tp^{Ph}K produced the octahedral complex 19, which contained an agostic B–H–M bond, rather than the expected B–N bond to the third 3-Phpz group. The reason for this is clearly steric, as the Tp^{iPr,4Br} ligand has two of the angles between the pz planes spread out to accommodate the phenyl groups, and the third angle is compressed, leaving only enough room for an agostic bond. There is no agostic interaction in the five-coordinate complex Tp^{iPr,4Br}Co[$Ph_2B(pz)_2$].[41]

The ligand [B(3-Pr^{i}pz)$_4$]$^-$, easily prepared from 3-isopropylpyrazole and KBH_4 under more drastic conditions than Tp^{iPr}, exhibits unusual coordinative behavior. It forms neither tetrahedral [B(3-Pr^{i}pz)$_4$]MX, nor octahedral [B(3-Pr^{i}pz)$_4$]$_2$M complexes. Instead, a series of isomorphous [B(3-Pr^{i}pz)$_4$]$_2$M complexes 20 is produced (M = Fe, Co, Ni, Cu, Zn), in which the ligand is bidentate, as was proved by X-ray crystallography.[39] Mössbauer spectra of [B(Pr^{i}pz)$_4$]$_2$Fe, measured between 85 and 296 K, revealed the presence of two quadrupole doublets, consistent with the presence of iron(II) in a distorted tetrahedral environment.[43]



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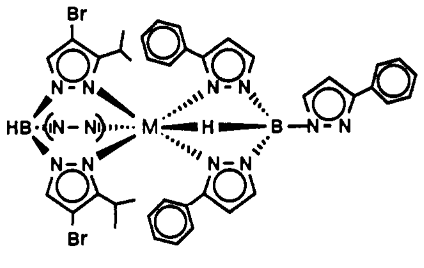

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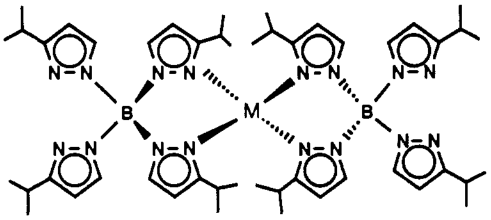

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8. Hydrotris(3-isopropyl-5-methylpyrazol-1-yl)borate [= *HB(3-Pr^i-5-Mepz)$_3$ = Tp^{iPr,Me}*]

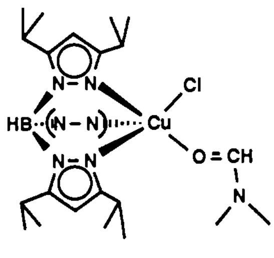
Unlike the reactions of hitherto mentioned asymmetric pyrazoles with KBH_4, which proceeded regiospecifically, producing a single homoscorpionate isomer, the reaction of 3-isopropyl-5-methylpyrazole gave a mixture of ligands, with about 80% of Tp^{iPr,Me} and about 20% of [HB(3-Pr^i-5-Mepz)$_2$(3-Me-5-Pr^{i}pz)]. This composition did not change even on prolonged high-temperature equilibration of the K salt with excess 3-isopropyl-5-methylpyrazole. This may reflect the relative rates of B–N bond formation at the nitrogen atoms next to methyl and next to the freely rotating isopropyl group. Nevertheless, the major isomer could be isolated through repeated recrystallization of derivatives. The bulky Tp^{iPr,Me}MoI$_2$NO complex, obtained initially as a mixture of isomers, rearranged on heating to a single isomer, [HB(3-Pr^i-5-Mepz)$_2$(3-Me-5-Pr^{i}pz)]MoI$_2$NO. Dialkoxy derivatives, Tp^{iPr,Me}MoNO(OR)$_2$ were obtained directly as single isomers.[44] The structure of Tp^{iPr,Me}MoNO(OEt)$_2$ was established by X-ray crystallography.[45]

9. Hydrotris(3,5-diisopropylpyrazol-1-yl)borate [= *HB(3,5-Pr$^i_2$pz)$_3$ = Tp^{iPr2}*]

The ligand Tp^{iPr2}K was prepared from KBH_4 and 3,5-diisopropylpyrazole. In contrast to Tp^{iPr} or Tp^{4BriPr}, where the isopropyl group straddles the pz plane with the methyls pointing either toward the metal (as in Tp^{iPr}CoNCS) or away from the metal (as in TpCoTp^{4BriPr}), in all hitherto reported Tp^{iPr2} complexes the isopropyl methyl groups point toward the 4-H. The symmetrical substitution with isopropyl groups precludes rearrangements observed with Tp^{iPr}, Tp^{iPr,4Br}, and Tp^{iPr,Me} which would, anyway, be degenerate.

Much of the Tp^{iPr2} coordination chemistry deals with copper. The $Tp^{iPr2}Cu$ complex, obtained from $Tp^{iPr2}K$ with CuCl, bonds to CO, yielding $Tp^{iPr2}CuCO$, which, unlike $Tp^{Ph2}CuCO$, reacts with triphenylphosphine, yielding $Tp^{iPr2}CuPPh_3$.[37]

The ligand Tp^{iPr2} readily formed tetrahedral $Tp^{iPr2}CuCl$ upon reaction with $CuCl_2$. The structure of $Tp^{iPr2}CuCl$, and of its readily formed five-coordinate DMF adduct **21**, was established by X-ray crystallography. Treatment of $Tp^{iPr2}CuCl$ with NaSR caused reduction of the former, but $Tp^{iPr2}CuSBu^t$ could be prepared by the reaction of $HSBu^t$ with the dinuclear $[Tp^{iPr2}CuOH]_2$.[46] This complex was claimed to have the closest resemblance in its type 1 CT and ESR spectral features, as compared with the actual enzyme.[47]



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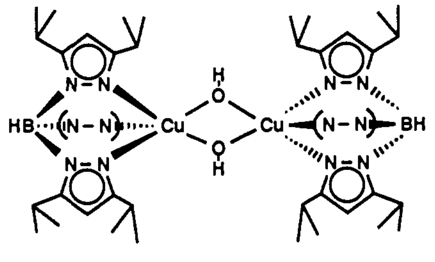

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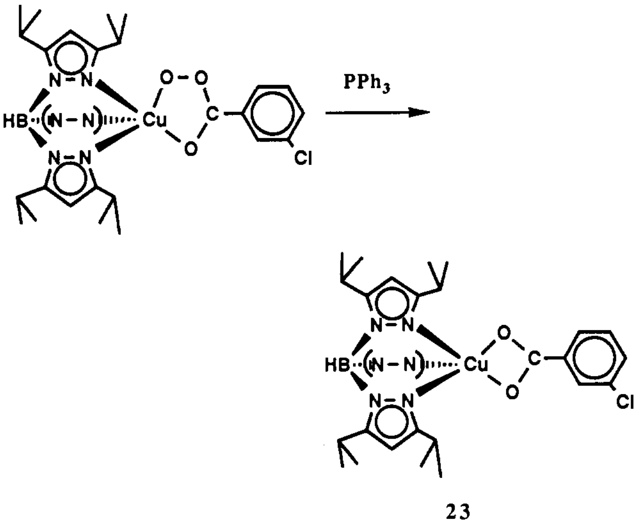
The antiferromagnetic complex $[Tp^{iPr2}CuOH]_2$ **22**, obtained from $Tp^{iPr2}CuBr$ and NaOH, was a useful starting material for a number of novel complexes. It reacted with *m*-chloroperbenzoic acid to yield a perbenzoate derivative, which was deoxygenated with triphenylphosphine, leading to the *m*-chlorobenzoate derivative **23**, the structure of which was established by X-ray crystallography,[48] as was that of the tetrahedral $Tp^{iPr2}CdI$.[28]



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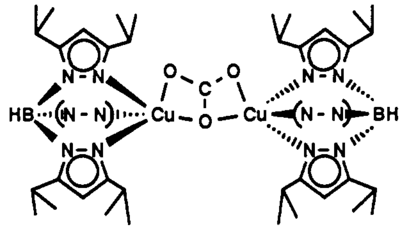
The dinuclear compound $[Tp^{iPr2}CuOH]_2$ reacts with atmospheric CO_2, yielding the carbonate complex **24**, the structure of which was determined by X-ray crystallography.[49]



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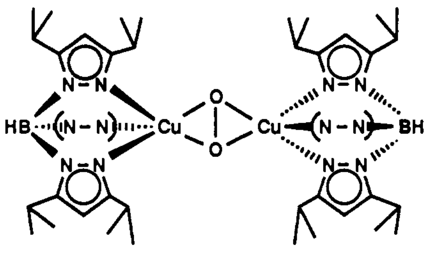
$[Tp^{iPr2}CuOH]_2$ can be converted with H_2O_2 to the μ-η^2:η^2-peroxo dinuclear copper(II) complex **25**, which is also accessible by the reaction of O_2 with $Tp^{iPr2}Cu$. The structure of **25**, containing the unusual side-on bridging by O_2, was confirmed by X-ray crystallography.[50] A detailed study of this complex, in view of its similar magnetic and spectroscopic properties to those of hemocyanin, led to a proposal of a new model for dioxygen binding in hemocyanin.[51]



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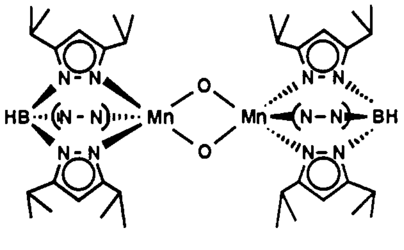
The dinuclear complex $[Tp^{iPr2}MnOH]_2$, with a structure analogous to that of the dinuclear copper complex **22**, was prepared by treating the five-coordinate complex $Tp^{iPr2}MnCl(H3,5\text{-}Pr^i{}_2pz)$ with NaOH. Oxidation of $[Tp^{iPr2}MnOH]_2$ with either $KMnO_4$ or O_2 afforded the dark red $Tp^{iPr2}Mn(\mu\text{-}O)_2MnTp^{iPr2}$ (**26**), containing Mn(III), the structure of which was established by X-ray crystallography.[52] While the anaerobic reaction with $KMnO_4$ produced only $Tp^{iPr2}Mn(\mu\text{-}O)_2MnTp^{iPr2}$, oxidation with oxygen yielded two types of Mn(III) complexes, the already described $Tp^{iPr2}Mn(\mu\text{-}O)_2MnTp^{iPr2}$ and a complex **27**,containing the $Tp^{iPr2}Mn\text{–}O\text{–}MnTp^{iPr2}$ core, but also with additional Mn–O bridges from each Mn to one isopropyl carbon per Tp^{iPr2} ligand.[53] This was regarded as a dioxygenase-type oxidation.

Replacement of chloride in $Tp^{iPr2}FeCl$ with benzoate ion produced the five-coordinate benzoate complex, which was still coordinatively unsaturated, binding oxygen reversibly, and which added pyridine or acetonitrile forming octahedral complexes. The complex with acetonitrile **28** was crystallographically characterized.[54]

Also synthesized and structurally characterized was the very oxygen-sensitive $(Tp^{iPr2}Fe)_2(\mu\text{-}OH)_2$ and $(Tp^{iPr2}Fe)_2(\mu\text{-}OH)_2$.[55] The oxygen chemistry of $Tp^{iPr2}Cu$- and $Tp^{iPr2}Fe$-derived species was summarized in a brief review.[56] The complex $Tp^{iPr2}Zn(OH)$ was converted via cleavage of tris- or bis-phosphate esters to the



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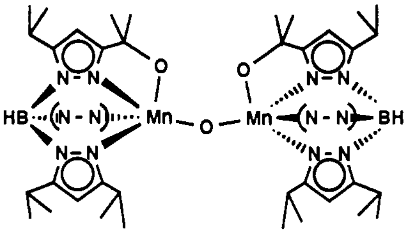

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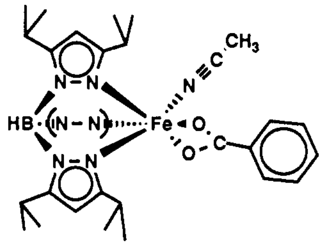
structurally characterized dinuclear, phosphate-bridged (Tp$^{\mathrm{iPr2}}$Zn)$_2$(μ-ArOP(O)O$_2$) and to related monomeric complexes.[57]



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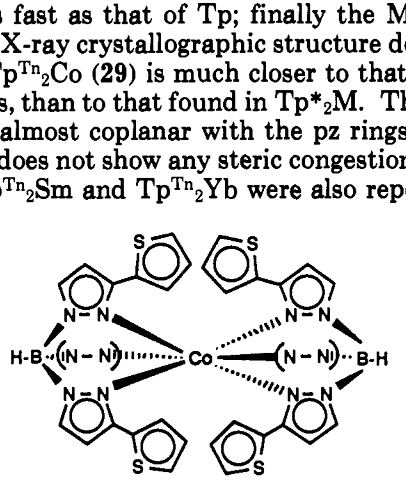
10. Hydrotris[3-(2-thienyl)pyrazol-1-yl]borate [= HB(3-Tnpz)$_3$ = Tp^{Tn}]

The ligand Tp$^{\mathrm{Tn}}$ shows much more resemblance in its coordination behavior to Tp than to Tp$^{\mathrm{Ph}}$. The complexes Tp$^{\mathrm{Tn}}{}_2$M are formed very readily, while attempts to prepare tetrahedral Tp$^{\mathrm{Tn}}$MX species produced Tp$^{\mathrm{Tn}}{}_2$M only. The rate of reaction with Tp$^{\mathrm{iPr,4Br}}$MCl is as fast as that of Tp; finally the M–N bond distance (X-ray crystallographic structure determination) of Tp$^{\mathrm{Tn}}{}_2$Co (**29**) is much closer to that in Tp$_2$M complexes, than to that found in Tp*$_2$M. The thienyl rings are almost coplanar with the pz rings, and the molecule does not show any steric congestion.[58] Complexes Tp$^{\mathrm{Tn}}{}_2$Sm and Tp$^{\mathrm{Tn}}{}_2$Yb were also reported.[36]



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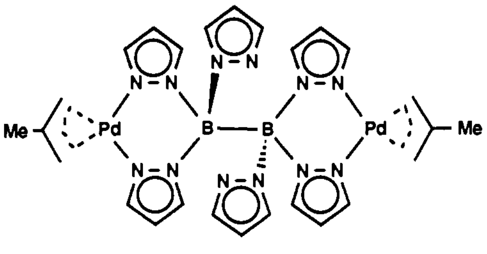
11. Bis[tris(pyrazol-1-yl)borate(B-B) [= (pz)$_3$BB(pz)$_3$ = (Tp)$_2$]

This unusual bis-tridentate ligand, which is essentially two Tp ligands joined through the boron atoms, has been prepared by heating (Me$_2$N)$_2$BB(NMe$_2$)$_2$, pyrazole, and Kpz. The two Tp sides coordinate independently. With divalent transition metals, intractable octahedral polymers are formed,[59] while endcapping with [ClPd-η^3-CH$_2$CMeCH$_2$] yields the monomeric [(η^3-CH$_2$CMeCH$_2$)Pd(pz)$_3$B]$_2$ (**30**), which contains only two pz groups coordinating to Pd per Tp, as was shown by an X-ray crystallographic structure determination.[60] In solution, however, there is rapid exchange of the coordinated and uncoordinated pz groups in each Tp set, so that even at low temperature only one type of pz is seen in the NMR.



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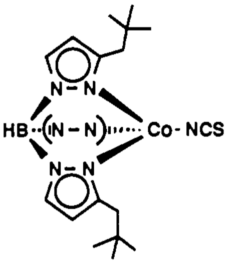
12. Hydrotris(3-neopentylpyrazol-1-yl)borate [= HB(3-neopentylpz)$_3$ = Tp^{Np}]

The ligand Tp$^{\mathrm{Np}}$ was synthesized as a halogen-free alternative to Tp$^{\mathrm{iPr,4Br}}$, in order to study, inter alia, reactions of LMX complexes with Grignard reagents and organolithium compounds without concerns about the 4-Br substituent. Compounds of type Tp$^{\mathrm{Np}}$MX were easily prepared, were stable, and readily produced heteroleptic Tp$^{\mathrm{Np}}$ML complexes, e.g. Tp$^{\mathrm{Np}}$CoTp. For steric reasons, the neopentyl group in tetrahedral Tp$^{\mathrm{Np}}$CoNCS (**31a** and **31b**) are oriented with the *tert*-butyl groups almost perpendicular to the pz plane, and all pointed either clockwise or counterclockwise, when viewed along the B–M axis. NMR spectra indicate equivalence of both methylene hydrogens, implying either completely free rotation of the neopentyl groups, or *synchronous* windshield-wiper-type wagging motion, making both hydrogens equivalent.[61]



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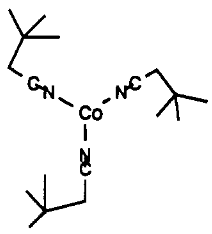
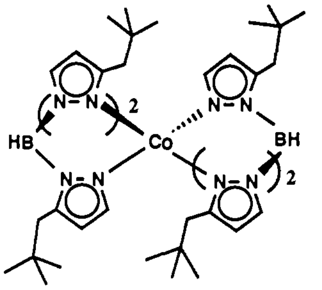


31b

In contrast to Tp$^{\mathrm{iPr}}$ and Tp$^{\mathrm{iPr,4Br}}$, unrearranged Tp$^{\mathrm{Np}}{}_2$M complexes could be isolated. The structure of Tp$^{\mathrm{Np}}{}_2$Ni, established by X-ray crystallography, is octahedral. The equatorial compression of the six neopentyl groups twists them into a conformation where the *tert*-butyl groups are turned away from the metal, and the CH$_2$–CMe$_3$ bond is almost parallel with the pz plane. This, clearly strained, structure is relieved by 1,2-borotropic rearrangement upon melting or recrystallization of Tp$^{\mathrm{Np}}{}_2$Ni from a high-boiling solvent. The resulting rearranged-ligand complex, **32**, is very high-melting and thermally stable.

The unrearranged Tp$^{\mathrm{Np}}{}_2$Co complex is probably five-coordinate in the solid, and tetrahedral in solution. On



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heating it becomes octahedral, via ligand rearrangement, as does the complex Tp^{Np}_2Fe. All the rearranged octahedral complexes are isomorphous.[61]

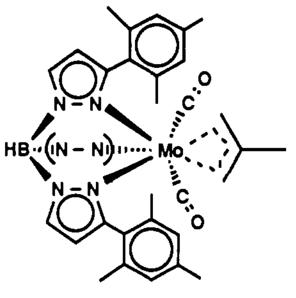
In its effective steric blocking, the neopentyl 3-substituent is very similar to 3-isopropyl, so that the steric hindrance hierarchy for Tp^R ligands is R = H < 2-thienyl < Me < Ph < iPr ≈ neopentyl < tBu.

13. Hydrotris[3-(trifluoromethyl)-5-methylpyrazol-1-yl]borate [= HB(3-CF$_3$-5-Mepz)$_3$ = $Tp^{CF_3,Me}$]

This ligand was prepared from 3-(trifluoromethyl)-5-methylpyrazole and KBH_4. It was used in synthesizing the complex $(\eta^2\text{-}Tp^{CF_3,Me})Ir(CO)(\eta^2\text{-}C_2H_4)$, which on heating in cyclohexane was converted to $(\eta^3\text{-}Tp^{CF_3,Me})Ir(CO)(H)(CH{=}CH_2)$, a rare instance where a hydridovinyl complex was more stable than its η^2-ethylene isomer. This finding contrasts with the related $Tp^*Rh(CO)(H)(CH{=}CH_2)$, which is easily isomerized to the complex $(\eta^2\text{-}Tp^*)Rh(CO)(\eta^2\text{-}C_2H_4)$.[62]

14. Hydrotris(3-mesitylpyrazolyl-1-yl)borate [= HB(3-mesitylpz)$_3$ = Tp^{Ms}]

To prevent or restrict rotation of a planar aromatic substituent in the 3-position of a Tp ligand, homoscorpionate ligands were prepared containing 2,6-substituents on the 3-phenyl which would prevent coplanarity with the pz ring (possible with R = phenyl), and which would tend force the phenyl ring to be orthogonal to the pz plane. This would eliminate complications arising from oxidative addition of the 3-phenyl group to a coordinatively unsaturated metal. One such ligand was Tp^{Ms}, prepared from KBH_4 and 3-mesitylpyrazole. Tp^{Ms} was characterized as the Tl salt, and it was converted to tetrahedral derivatives, $Tp^{Ms}MX$, which did not produce crystals suitable for X-ray crystallography. However, the ligand structure was determined via the $Tp^{Ms}Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$ complex. The mesityl group is indeed nearly orthogonal to the pz plane.[63]



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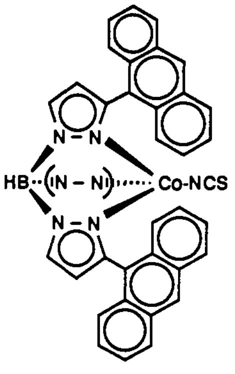
15. Hydrotris[3-(9-anthryl)pyrazolyl-1-yl]borate [= HB[3-(9-anthryl)pz]$_2$ = Tp^{Ant}]

Another ligand with an aromatic 3-substituent, orthogonal to the pz ring was Tp^{Ant}, containing a 9-anthryl group. It was prepared from KBH_4 and 3-(9-anthryl)pyrazole. The structures of several of its derivatives, $Tp^{Ant}Tl$, $Tp^{Ant}CoCl$, and $Tp^{Ant}CoNCS$ (**34**) were determined by X-ray crystallography. In all of them the anthryl group was almost orthogonal to the pz plane, but total orthogonality was prevented by nonbonding interactions of the 2,3- and 6,7-hydrogens. The anthryl groups provide extensive side shielding of the metal, but, at the same time, permit considerable frontal access.[64]



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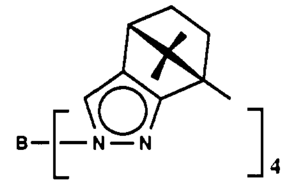
16. Optically Active Poly(pyrazolyl)borates

a. Tetrakis(camphorpyrazolyl)borate. The optically active sodium salt of tetrakis(4,5,6,7-tetrahydro-7,8,8-trimethyl-2*H*-4,7-methanoindazolyl)borate [(= $NaB(camphpz)_4$), **35**] was prepared from camphorpyrazole and $NaBH_4$ and was converted to the $B(camphpz)_4$-CuCO derivative. The Na Salt and the CuCO derivative were used in enantioselective cyclopropanation of styrene with ethyl diazoacetate, catalyzed by Cu(I), Cu(II), and Rh(I).[65] In an attempt to prepare $KHB(camphpz)_3$, only an inseparable mixture of products was obtained.[66]



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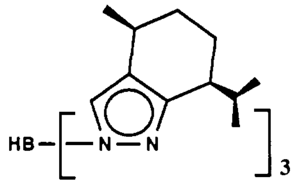
*b. Hydrotris(2R,5R-menthylpyrazolyl)*borate (= Tp^{Menth}). The enantiomerically pure homoscorpionate ligand Tp^{Menth} (**36**) was prepared from (2*R*,5*R*)-menthylpyrazole and KBH_4, and it was converted to complexes $Tp^{Menth}MCl$ (M = Zn, Ni, Cu, Co), $Tp^{Menth}M(OAc)$ (M = Cu and Ni), and $Tp^{Menth}M(NO_3)$ (M = Cu, Ni). The structure of the tetrahedral $Tp^{Menth}ZnCl$ was determined by X-ray crystallography.[67]



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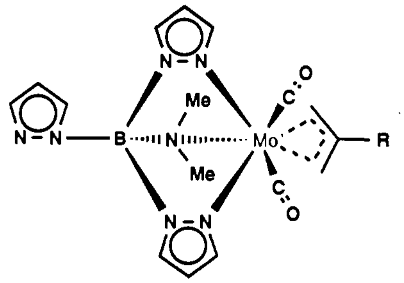
17. Miscellany

It has been noted[68] that heating KBH_4 with 3 equiv of 5-aminoindazole at <100 °C, yields hydrotris(5-

aminoindazolyl)borate, isolated as the black (sic) Tl salt and that a number of metal derivatives of this ligand have been prepared.

B. Heteroscorpionates

An unusual ligand which has the potential to coordinate either as a homoscorpionate, or as a heteroscorpionate is [(Me$_2$N)B(pz)$_3$]$^-$. It was prepared by the reaction of B(NMe$_2$)$_3$ with pyrazole at room temperature, being obtained as the free acid [(Me$_2$N)B(pz)$_3$]H. The Mo(CO)$_2$(η^3-allyl) derivatives, such as **37**, were prepared and characterized by variable-temperature NMR, which proved the ligand acted as a heteroscorpionate, coordinating via two pz groups, and through the NMe$_2$, rather than through the available third pz group.[69]



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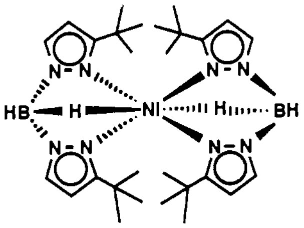
Some unusual coordination chemistry was observed with heteroscorpionate ligands H$_2$B(3Bu^{t}pz)$_2$. In the complex [H$_2$B(3Bu^{t}pz)$_2$]$_2$Ni (**38**), the metal is octahedrally coordinated, including two agostic B–H–Ni bonds, as was established by X-ray crystallography. The agostic bonding is probably caused by the very deep boat structure adopted, which minimizes nonbonding tBu–tBu interactions.[70] The compound H$_2$B(3-Bu^{t}pz)$_2$AlMe$_2$ (**39**), prepared from the K salt and Me$_2$AlCl, undergoes ligand rearrangement to **40** at 100 °C, as shown below:[15]



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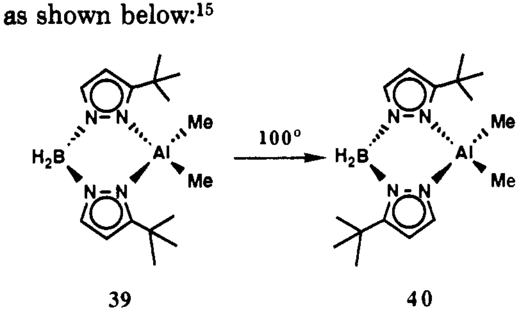
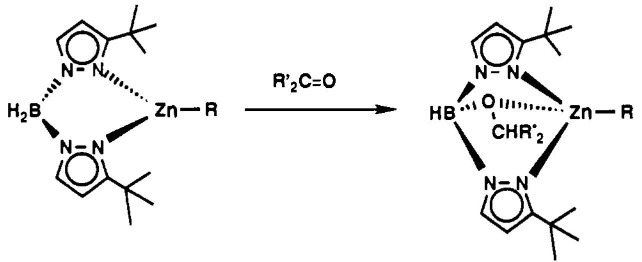


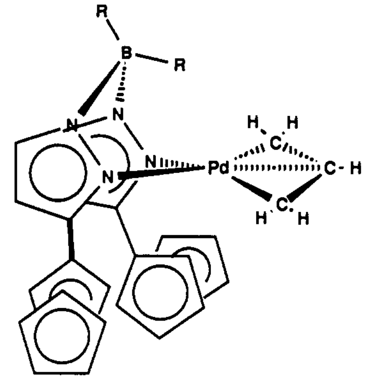
39 40

Unusual monomeric, three-coordinate zinc–alkyl complexes **41** [H$_2$B(3-Bu^{t}pz)$_2$ZnR (R = Me, Et, t-Bu)] were prepared from H$_2$B(3-Bu^{t}pz)$_2$Tl and ZnR$_2$, and the structure of H$_2$B(3-Bu^{t}pz)$_2$ZnBu^t was established by X-ray crystallography. While protic reagents, HX, yield RH and H$_2$B(3-Bu^{t}pz)$_2$ZnX, aldehydes and ketones react at the BH$_2$, producing the probably tetrahedral complexes **42**.[71] The H$_2$B(3-Bu^{t}pz)$_2$ZnOH derivative exists as a trimer with a [ZnO]$_3$ core.



41 42

The reaction of 3-ferrocenylpyrazole with KBH$_4$ was used to prepare the heteroscorpionate ligand, H$_2$B(3-ferrocenylpz)$_2$ which was characterized as the Tl salt. The ligand HB(3-ferrocenylpz)$_3$ could not be prepared in this fashion, due to the decomposition of the ferrocenyl moiety. The dialkyl ligands, R$_2$B(3-ferrocenylpz)$_2$, were prepared by the reaction of 3-ferrocenylpyrazole with Me$_2$NBR$_2$ (R = Et, R$_2$ = cyclooctane-1,5-diyl), yielding the "free acids", [R$_2$B(3-ferrocenylpz)$_2$H, converted to their Na salts via reaction with NaH. These ligands formed Pd–π-allyl complexes **43**, characterized by ^{1}H and ^{13}C NMR.[72]

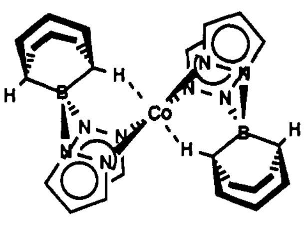


43

(Fe atoms in ferrocenyl substituents are hidden.)

A heteroscorpionate ligand, R$_2$B(pz)$_2$, in which the R$_2$B grouping was part of a rigid cage structure, such that only the single bridgehead hydrogen would be pointed at the metal, was prepared from borabicyclononane, Hpz, and Kpz. This ligand, BBN(pz)$_2$, yielded with Co(II) an octahedral complex **44**, containing two agostic C–H–Co bonds (H–Co distance 2.166 Å), as was confirmed by an X-ray crystallographic structure determination.[73,74] The agostic C–H–Co bond is also characterized by a sharp IR stretch at 2690 cm^{-1}, which was the lowest frequency among related [BBN(pz)$_2$]$_2$M complexes (M = Cu, Ni, Zn). The ligand-field spectra, room-temperature EPR spectra, and magnetic susceptibility of [BBN(pz)$_2$]$_2$Co were determined.[75] By contrast, in the heteroleptic complex **45**, the analogous Co–H distance is much longer (2.61 Å) due to the repulsive forces of the three isopropyl groups, and there is no agostic C–H–Co interaction.[74]

A series of BBN(pz)$_2$M(CO)$_2$(η^3-CH$_2$CRCH$_2$) complexes (M = Mo, W; R = H, Me, phenyl) was synthesized. Presence of an agostic C–H–M bond in these compounds was indicated by ^{1}H NMR peaks in the −4.1 to −5.2 ppm range. The Mo complexes



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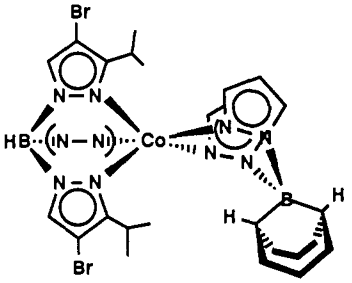


45

exhibited greater shifts than their W analogs, and the shift increase as a function of R was H > phenyl > Me.[74]

The reaction of BBN with 3-substituted pyrazoles and pyrazolide ions yielded ligands [BBN(3Rpz)$_2$] from which a series of rhodium complexes BBN(3Rpz)$_2$Rh(LL) was prepared (R = H, Me; LL = 2 CO; 1,5-cyclooctadiene; norbornadiene). These compounds were characterized by one- and two-dimensional NMR and by ^{1}H NOESY spectroscopy. An X-ray structure determination of BBN(3Rpz)$_2$Rh(COD) showed the Rh to be 2.42 Å away from the bridgehead hydrogen. The C–H–Rh interaction is a weak one, but sufficient to cause considerable deshielding of the bridgehead H and to possibly contribute to the lack of inversion of the B(pz*)$_2$Rh ring, which is observed in analogous Ph$_2$B(pz)$_2$Rh(LL) complexes.[76]

III. Complexes of Previously Reported Scorpionate Ligands

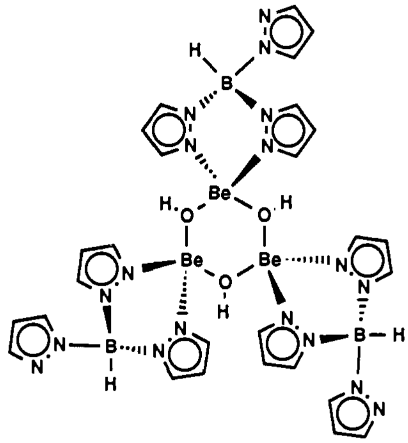
A. Homoscorpionates

1. General

The whole series of ligands, Tp, pzTp, and H$_2$B(pz)$_2$ was studied in detail by ^{1}H, ^{13}C, ^{15}N, and ^{11}B NMR spectroscopy, which permitted unambiguous assignment of the 3, 4, and 5 protons and carbons in the pz ring. Structures of the isomorphous pzTpK and pzTpNa were determined by X-ray crystallography.[77] The electronic structure of a series of isostructural Tp$_2$M complexes (M = Fe, Co, Ni, Cu and Zn) was studied by means of He I and He II photoelectron spectroscopy.[78] The ligands Tp, pzTp, Tp*, and H$_2$B(pz)$_2$ were used in studies of extraction into chloroform of divalent alkaline earth ions as the respective bis-complexes.[79,80] Complexes pzTp$_2$Fe, pzTp$_2$Cu, and [H$_2$B(pz)$_2$]$_2$Cu were used in a study of nonaqueous on-line simultaneous determination of metals by size exclusion chromatography, with inductively coupled plasma atomic emission spectrometric detection.[81] Average bond lengths for a large number of poly(pyrazolyl)borate complexes of the *d*- and *f*-block metals have been compiled.[82]

2. Group IIA: Be, Mg

Two novel beryllium complexes were prepared from Tp and pzTp ligands and aqueous BeCl$_2$ and had their structures determined by X-ray crystallography. The [B(pz)$_4$]$_2$Be complex contains tetrahedrally coordinated Be, and the ligands are bidentate. By contrast, the product from the Tp reaction, TpBeOH, has the trimeric structure **46**, containing a [BeO]$_3$ core, which contain hydrogen bonds between the uncoordinated pz and the bridging OH groups.[83]



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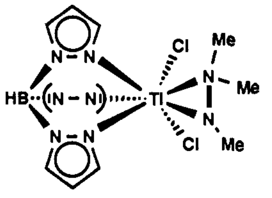
The Tp*MgR derivatives (R = Me, Et, iPr, nBu, tBu, phenyl, and vinyl) undergo ligand redistribution reactions, yielding Tp*$_2$Mg. This contrasts with the stability of their Tp^{tBu}MgR analogs.[84]

3. Group IVB: Ti, Zr, Hf

The readily prepared TpTiCl$_3$ and Tp*TiCl$_3$ complexes served as starting materials for a variety or other Ti derivatives. While TpTiCl$_3$ reacted with hydrazines producing Ti(III) complexes containing the [TpTiCl$_3$]$^-$ anion, e.g. [NHMe$_2$NHMe]$^+$[TpTiCl$_3$]$^-$, which was structurally characterized, the reaction of Tp*TiCl$_3$ yielded a hydrazine-free complex, which proved to be the octahedral Tp*TiCl$_2$(3,5-Me$_2$pz).[85] Subsequently, complexes TpTiCl$_2$(Me$_2$NNMe) and TpTiCl$_2$(PhNNH$_2$) were produced and structurally characterized. They contain the hydrazido(1-) moiety bonded sideways, as in **47**.[86]



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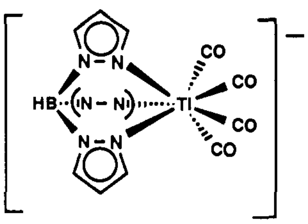


48

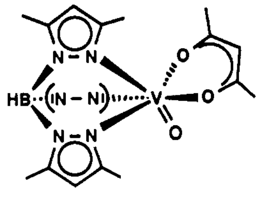
The monoanion **48** was prepared via displacement of Me$_2$PCH$_2$CH$_2$PMe$_2$ (dmpe) by Tp (Tp* was unreactive) from Ti(CO)$_5$(dmpe) and was isolated as the Et$_4$N salt. This derivative of Ti(CO)$_7$ is remarkably stable to air oxidation and represents the first example of N-coordinated zerovalent titanium.[87] Titanium complexes Tp*Ti(OR)Cl$_2$, Tp*Ti(OR)$_2$Cl, and Tp*Ti(OR)$_3$ were synthesized and were used to obtain the alkyltitanium compounds of structure Tp*Ti(OR)Me$_2$, Tp*Ti(OR)$_2$Me, and Tp*Ti(OR)CH$_2$SiMe$_3$ via reaction with the appropriate Grignard reagents.[88] A catalyst for the polymerization of ethylene was prepared, on the basis of the reaction of Tp (and of other polypyrazolylborates) with Ti or Zr compounds and aluminum alkyls.[89]

Air- and moisture-stable zirconium complexes $Tp^*Zr(OAr)_3$, where Ar is a substituted phenyl group (H, 3-NO_2, 4-NO_2, 2-F, 4-F, 4-tBu) were prepared by chloride displacement from Tp^*ZrCl_3 with the appropriate alkoxide ion.[90] In this reaction all three chlorides are replaced by unhindered aryloxy groups. With hindered phenoxides, such as 2,6-dimethyl- or 2,6-diphenylphenoxide, it is possible to obtain $Tp^*ZrCl(OAr)_2$ and $Tp^*ZrCl_2(OAr)$ species. Several of these complexes were characterized by X-ray crystallography and were found to contain octahedrally coordinated Zr.[91] The free acid, HTp, displaced one Cp group from Cp_2ZrCl_2 or from Cp_2HfCl_2, yielding $TpMCpCl_2$, in which both chlorides could be replaced with aryloxy groups. The structure of $TpZrCp(2\text{-phenylphenoxy})_2$ was determined by X-ray crystallography.[92] It contains η^3-Tp, η^3-Cp, and two symmetrically inequivalent 2-phenylphenoxide ligands.[93] The synthesis of complexes $TpZrCl_2(Cp)$ and $Tp^*ZrCl_2(Cp)$ has been reported.[94]

4. Group VB: V, Nb, Ta

Heteroleptic oxovanadium complexes Tp*VOL (L = acac or R_2NCS_2) were prepared by acac displacement from $VO(acac)_2$, and they were characterized by electronic spectra and by ESR parameters, which suggest a trigonally distorted octahedral structure.[95,96] This was confirmed by an X-ray crystallographic structure determination of $Tp^*VO(S_2CNPr_2)$.[97] A similar structure was found in Tp*VO(acac) (**49**).[98]

Additional structures determined by X-ray crystallography were $Tp^*VCl_2(DMF)$, Tp*VOCl(DMF), Tp^*VOCl_2, and $Tp^*VCl_2(3,5\text{-}Me_2pzH)$. In all these structures the metal is octahedral and Tp* ligand is tridentate. Surprisingly, in Tp^*VOCl_2 (**50**), the Tp* ligand is bidentate, and the metal adopts a square-pyramidal geometry.[99] More detailed studies of the above compounds, characterized by molar conductance, electrochemistry, magnetic properties, UV–visible spectra, and ESR, were carried out, comparing complexes derived from Tp and from Tp*. The structure of $[Tp_2V][BPh_4]$ was determined by X-ray crystallography; the cation is octahedral with V–N bonds ranging from 2.055 to 2.095 Å.[100]



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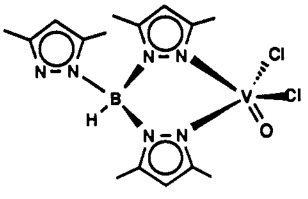

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A series of vanadium(V) phenolate complexes of structure $Tp^*VO(4\text{-R-phenoxy})_2$, where R = H, Br, NO_2, OMe, and tBu, has been prepared from Tp*VOCl(DMF) and the appropriate phenoxide ion. The structure of $Tp^*VO)(4\text{-bromophenoxy})_2$ was determined by X-ray crystallography, which showed octahedral coordination, with tridentate Tp*. The phenoxy group can be hydrolyzed off, yielding the dimeric complex $[Tp^*VO(OAr)]_2O$.[101] The green complex $Tp^*V(\mu\text{-O})(\mu\text{-OAc})VTp^*$ has been prepared from $Tp^*VCl_2(DMF)$ and acetate ion. Its electronic spectra and magnetic properties were determined.[102]

Reaction of Tp*K with $NbCl_3(DME)$(1-phenylpropyne) produced in high yield the complex $Tp^*NbCl_2(HC{\equiv}CPh)$, the structure of which was determined by X-ray crystallography. The molecule contains the $HC{\equiv}CPh$ ligand in the mirror plane, with the phenyl group fitting between two pz planes. Spectroscopy suggests that it is acting as a four-electron donor. ^1H and ^{13}C NMR spectra show the presence of two isomers and give no evidence of isomer interconversion in solution up to 100 °C.[103]

5. Group VIB: Cr, Mo, W

Complexes of group VIB metals, especially Mo and W, with homoscorpionate ligands Tp and Tp*, have been studied very extensively. Papers dealing with derived compounds comprise 44% of all Tp and Tp* studies. Some of the studies use Tp and Tp* as stabilizing capping ligands, other use them to substitute for three histidine residues in enzyme models, still others take advantage of them as molecular vises in strongly "holding" the metal ion, while operations are performed at the open coordination sites.

Chromium(III) derivatives $TpCrCl_2py$, $TpCrCl_2(Hpz)$, $[TpCrCl_3]AsPh_4$, and $[Tp_2Cr]PF_6$ have been synthesized, and the structure of $TpCrCl_2py$ was determined by X-ray crystallography. The coordination is octahedral, and the pyridine plane is bisecting the angle between two pyrazole rings.[104] Electrochemistry of $[TpM(CO)_3]^-$ species (M = Cr, Mo, W) was studied, and their IR spectra were compared with those of related complexes.[105] The radicals $TpCr(CO)_3$, $Tp^*Cr(CO)_3$, $pzTpCr(CO)_3$, and the complex $TpCr(CO)_2(PMe_3)$ were synthesized and characterized. EPR spectra of these radicals were compared with those of the Mo analogs.[106]

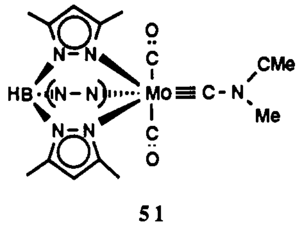
A large percentage of homoscorpionate–molybdenum chemistry originates from the readily available $[TpMo(CO)_3]^-$ and $[Tp^*Mo(CO)_3]^-$ anions. The heat of reaction of Tp with (toluene)$Mo(CO)_3$ and the heat of ligand exchange has been determined.[107] In addition to displacement of CO by other ligands, the $[TpMo(CO)_3]^-$ anion can be oxidized by a variety of mild oxiding agents to a remarkably stable radical $TpMo(CO)_3$, the structure of which was established by X-ray crystallography. EHMO and ^1H NMR studies show that the odd electron occupies a doubly degenerate orbital and that it is delocalized onto the pz rings of Tp. The radical $TpMo(CO)_3$ can be decarbonylated, forming a dinuclear species, containing a triply bonded Mo core.[108] A similar radical was prepared from $[Tp^*Mo(CO)_3]^-$ upon oxidizing it with Cp_2Fe^+. The radical reacted with sulfur, forming the species $[Tp^*Mo(CO)_2]_2S$.[109,110]

The pK_a values for the acids $TpMo(CO)_3H$ and $Tp^*Mo(CO)_3H$ were found to be 11.3 and 10.2, respectively, in acetonitrile. Rates of degenerate electron transfer between $[Tp^*Mo(CO)_3]^-$ and $Tp^*Mo(CO)_3H$ were determined, as were the rates of degenerate proton transfer between $Tp^*Mo(CO)_3H$ and $Tp^*Mo(CO)_3$ and the rates of degenerate hydrogen atom transfer between $Tp^*Mo(CO)_3H$ and $Tp^*Mo(^{13}CO)_3$. The electron transfer was very fast, proton transfer was slow, and hydrogen atom transfer slower yet. The structures of $Tp^*Mo(CO)_3H$ and $Tp^*Mo(CO)_3$ were established by X-ray crystallography. While the $Tp^*Mo(CO)_3$ radical is of C_{3v} symmetry, $Tp^*Mo(CO)_3H$ has a four-legged piano-stool structure with a short Mo–H bond (1.44 Å).[111] In related work, the energetics of deprotonation and metal–hydrogen bond homolysis of TpMo(CO)$_3$H and Tp*M(CO)$_3$H (M = Cr, Mo, W) and of their cation radicals were studied by the thermochemical cycle method. Oxidation led to a weakening of the M–H bond by 108–117 kJ/mol toward deprotonation and by 25–34 kJ/mol toward homolysis.[112]

Cationic tungsten(II) complexes [Tp*W(CO)$_3$L][PF$_6$], where L = PMe$_3$, PEt$_3$, PMe$_2$Ph and PPh$_3$, were prepared from the Tp*W(CO)$_3$ radical by oxidation with Cp$_2$Fe$^+$, followed by addition of the phosphine. Complexes with L = PMe$_3$ and PMe$_2$Ph were characterized by X-ray crystallography and were found to have a 3:3:1 capped octahedron structure, while the PPh$_3$ complex had the 4:3 piano-stool geometry.[113]

Treatment of TpMo(CO)$_2$(η^4-1,3-cyclohexadiene) and Tp*Mo(CO)$_2$(η^4-1,3-cyclohexadiene) with single-electron donors resulted in the formation of π-allyl complexes TpMo(CO)$_2$(η^3-cyclohexenyl) and Tp*Mo(CO)$_2$(η^3-cyclohexenyl). By contrast, an analogous reaction of TpMo(CO)$_2$(η^4-1,3-cycloheptadiene) yields, in addition to TpMo(CO)$_2$(η^3-cycloheptenyl), TpMo(CO)$_2$(4,5-dehydro-η^3-cycloheptenyl).[114]

Complexes TpMo(CO)$_2$(η^2-COR) are formed from TpMo(CO)$_3^-$ upon reaction with MeI, Me$_3$O$^+$, MeCOBr, or PhCOBr. Structures of TpMo(CO)$_2$(η^2-COMe), TpMo(CO)$_2$(η^2-COPh), TpMo(CO)(P(OMe)$_3$)(η^2-COMe), and TpMo(CO)(PEt$_3$)(η^2-COMe) were determined by X-ray crystallography; the various complexes were subjected to EHMO calculations.[5] The structure or a related complex, pzTpMo(CO)$_2$(η^2-OCNMe$_2$), was also determined.[115] It is isostructural, but not isomorphous with pzTpMo(CO)$_2$(η^2-SCNMe$_2$).[116] The TpMo(CO)$_3^-$ anions react with Br$_2$ or I$_2$ to yield seven-coordinate TpMo(CO)$_3$X species, which have a 3:4 piano-stool structure and which show dynamic C_{3v} symmetry down to −80 °C.[117] By contrast, Tp*Mo(CO)$_3$I is unstable, losing CO; the resulting Tp*Mo(CO)$_2$I adds tBuNC, forming Tp*Mo(CO)$_2$I(CNtBu), which upon treatment with Na/Hg produces the anion [Tp*Mo(CO)$_2$(CNtBu)]$^-$. This reacts with MeI yielding a mixture of molybdenum aminocarbyne, η^2-iminoacyl, and η^2-acyl complexes, **51**, **52**, and **53**, respectively. Only the aminocarbyne is formed in this reaction, when tBuNC is replaced by either MeNC or PhNC. Protonation of **51** with HBF$_4$ in the presence of phenylacetylene yields the η^2-vinyliminium complex, **54**, the structure of which was established by X-ray crystallography.[118]



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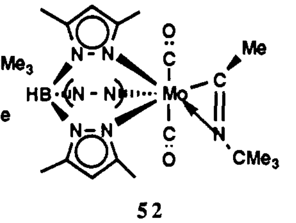

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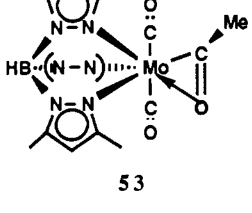

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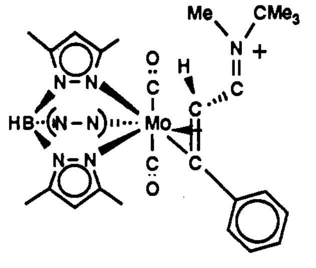
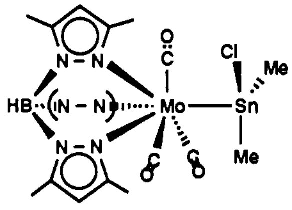


54

Unusual complexes, containing Mo–Sn or Mo–Cu bonds were prepared by the reaction of [TpMo(CO)$_3$]$^-$ and [Tp*Mo(CO)$_3$]$^-$ with R$_3$SnCl (R = Me, Ph), Me$_2$SnCl$_2$, [Cu(PPh$_3$)Cl]$_4$, and CuI(tmed). The products, TpMo(CO)$_3$SnPh$_3$, Tp*Mo(CO)$_3$SnMe$_2$Cl (**55**), and TpMo(CO)$_3$Cu(tmed) contain the Sn or Cu atom positioned on the B–Mo axis, as was established by X-ray crystallography.[119] The complex TpMo(CO)$_3$Rh(PPh$_3$)$_3$ was prepared similarly.[120] The trinuclear anion **56**, containing a linear array of Mo–Cu–Mo atoms, was obtained by the reaction of [Tp*Mo(CO)$_3$]$^-$ with CuI in the presence of 1 equiv of Ph$_2$CH$_2$CH$_2$PPh$_2$. The cation isolated in the product was {[Ph$_2$CH$_2$CH$_2$PPh$_2$]$_2$Cu}$^+$.[121]



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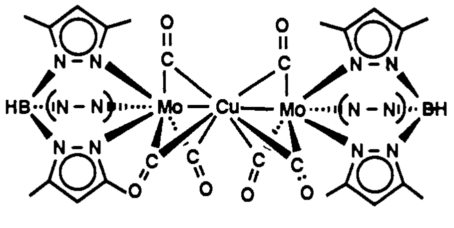
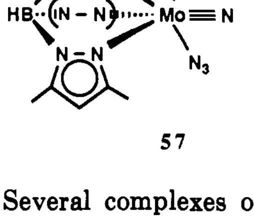


56

The hydrolytically rather stable molybdenum nitrido complexes, Tp*MoN(N$_3$)$_2$ (**57**), Tp*MoN(N$_3$)Cl (**58**), and Tp*MoNCl$_2$ were prepared and spectroscopically characterized, and the structures of the first two compounds were determined by X-ray crystallography. Compound Tp*MoN(N$_3$)$_2$ is slowly hydrolyzed to Tp*MoO$_2$N$_3$.[122,123]



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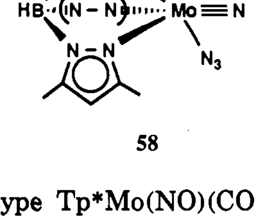
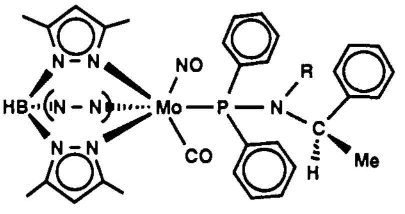


58

Several complexes of the type Tp*Mo(NO)(CO)(PPh$_2$R*) (**59**), where R* is a chiral substituent, as well as analogs containing Tp and pzTp instead of Tp*, were synthesized. They were found to exhibit diastereomer splitting in the ^{95}Mo NMR spectra, despite the structural similarity of the CO and NO ligands.[124] Tp*Mo(NO)X_2 reacted with (+)- and (−)-1-phenylethylamine, affording diastereomeric mixtures of the complex Tp*Mo(NO)X(NHCHMePh). The mixtures were separated by chromatography, and the structure of the pure diastereomer **60**, obtained from (+)-NH_2CHMePh was determined crystallographically. The absolute configuration was *S*.[125]



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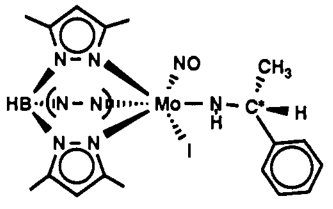

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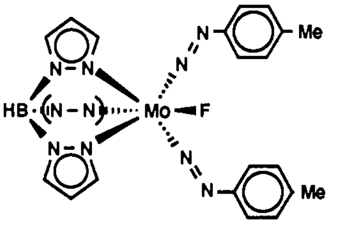
The bis-arylazo derivative, TpMoF(N=N-*p*-tolyl)$_2$ was prepared from TpTl and [CpMo(N=N-*p*-tolyl)$_2$(PPh$_3$)]BF$_4$, and its structure was determined by X-ray crystallography. The complex **61** is octahedral and contains singly bent arylazo groups.[126] The structure of a related compound **62** was also determined. This compound and related ones, containing other substituents on the phenyl ring, as well as TpW(NO)(N=NPh)Cl, were prepared by reacting ClNO with TpM(CO)$_2$(N=NAr),[127] as were complexes where the arylazo group was derived from 3,5-dimethylpyrazole-4-diazonium and 5-oxo-3-pyrazolin-4-diazonium salts, respectively.[128] The salt [TpMo(CO)(N=NPh)(PPh$_3$)]BF$_4$ was prepared, but was unstable.[129]



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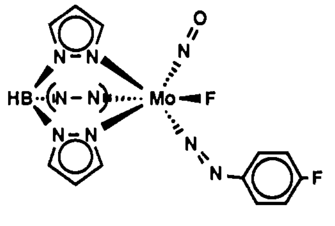
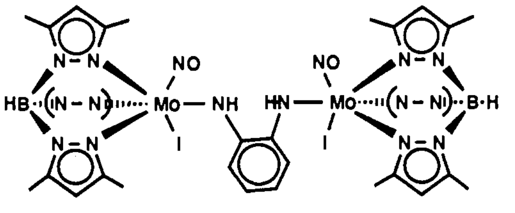


62

The complex Tp*MoNOI$_2$, obtained from Tp*MoNO(CO)$_2$, is an outstanding starting material for the synthesis of a wide array of very stable Tp*Mo(NO)XZ complexes and detailed procedures for such syntheses have been published.[130] A variety of new Tp*MoNO(OR)$_2$ and Tp*MoNO(OR)Cl complexes (R = noncyclic alkyl groups, some fluorinated) has been prepared and characterized.[131] Similarly, Tp*MoNO(OR)X and Tp*WNO(OR)X complexes were prepared (X = Cl, Br), where R contained cyclic ether structures.[132] Treatment of Tp*MoNO(OR)I, Tp*MoNO(SR)I, or Tp*MoNO(NHR)I with silver acetate or benzoate yielded products of iodide replacement by the carboxylato group, in a monodentate manner, as was proved by an X-ray crystallographic structure determination of Tp*MoNO(NHPh)(OAc).[133] Diastereomeric mixtures of complexes Tp*MoNO(OR)Cl and Tp*WNO(OR)Br (where OR was (+)- or (−)-menthoxide) were prepared and separated by chromatography. The structure of the diastereomer Tp*MoNO[(−)-menthoxide]Cl was determined crystallographically. The absolute configuration in this compounds was R, and those of the other complexes were related to it by comparison of their circular dichroism spectra.[134] Treatment of Tp*MoNOI$_2$ with oxacyclobutane, THF, or oxacycloheptane (but not oxacyclohexane) in the presence of moisture yields products resulting from ether ring opening: Tp*MoNO[O(CH$_2$)$_n$I]I.[135] The same ring opening occurred in the reaction of oxacyclobutane with Tp*MoNOX$_2$ (X = Cl or Br) or with Tp*WNOCl$_2$. In each case, the product was Tp*MNO[O(CH$_2$)$_3$X]X.[136]

The reaction of Tp*MoNO(NHR)I or of Tp*WNO(NHR)Cl with RNH$^-$ afforded complexes Tp*MNO(NHR)$_2$. Mixed alkylamido–arylamido complexes were also prepared, as were their bis-arylamido analogs. The structure of Tp*MoNO(NHBu)$_2$ was determined; it contains a linear NO ligand.[137] Upon treatment of Tp*MoNOI$_2$ with 2-aminopyridine, the Tp*MoNO(2-pyridylamido)$_2$ derivative was obtained, the structure of which showed no interaction of the pyridyl nitrogen with the electron-deficient metal. From 2-(aminomethyl)pyridine, the 17-electron diamino complex was obtained. The tungsten analogs were prepared similarly.[138] Pyrrolidine or piperidine yielded, with Tp*MoNOI$_2$, both monoamino and monoamido complexes. The structures of Tp*MoNO(NHC$_5$H$_{10}$)I and Tp*MoNO(NC$_4$H$_8$)I were determined; they were similar, but showed the Mo–amide bond to be much shorter than the Mo–amine bond (1.937(5) Å versus 2.241(6) Å).[139,140] While 1,2-phenylenediamine produced with Tp*MoNOI$_2$ the dinuclear complex **63**, toluene-3,4-dithiol gave the chelated derivative **64**. This compound was reduced at a more anodic potential than the unchelated analog, Tp*MoNO(SPh)$_2$.[141] The structure of the latter compound was determined by X-ray crystallography.[142]

Bridged dinuclear complexes of structure Tp*Mo(NO)I(NHC$_6$H$_4$NH)MoTp*(NO)(OR) and Tp*Mo(NO)(OR)NHC$_6$H$_4$NHMoTp*(NO)(OR) were prepared and spectroscopically characterized.[143] A different type of heterobimetallic complexes was obtained via the reaction of Tp*Mo(NO)X[NH(CH$_2$)$_3$PPh$_2$] with [Rh(CO)$_2$Cl]$_2$, HgI$_2$, and CdCl$_2$. In each case two molecules of Tp*Mo(NO)X[NH(CH$_2$)$_3$PPh$_2$] coordinated via the diphenylphosphine moiety, displacing one CO in the case the Rh complex. Also prepared were Tp*Mo(NO)I[*p*-OC$_6$H$_4$HgCl], Tp*Mo(NO)I[NHC$_6$H$_4$-Pd(PPh$_3$)$_2$Br], and Tp*Mo(NO)I[NHC$_6$H$_4$Pt(PPh$_3$)$_2$I]; the last two compounds via zerovalent [Pd(PPh$_3$)$_4$] and [Pt(C$_2$H$_4$)(PPh$_3$)$_2$].[144] A still different type of bi- and



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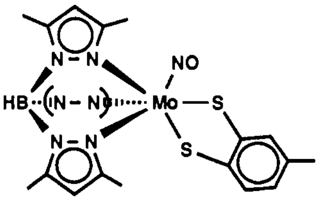

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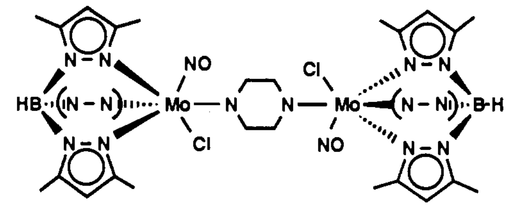
trimetallic complexes, containing both electron-releasing and electron-accepting redox centers was prepared via displacement of iodide ions from Tp*Mo(NO)I_2 by the anions of (hydroxymethyl)ferrocene, 1,1'-bis(hydroxylethyl)ferrocene, and 1,1'-bis(hydroxymethyl)ruthenocene. The last two gave rise to binuclear complexes; the first one produced a trinuclear compound. Electrochemical studies showed reversible reduction processes and lack of effect of replacement of Fe by Ru on the reduction potential of the Mo redox center.[145] The compound Tp*Mo(NO)(Cl)NH-C_6H_4-*p*-CH=CH—CH=CMe—CH=CH—CH=CMe—CH=CH—C_9H_{15}, based on a retinal derivative, was prepared. It showed no detectable second harmonic generation, when irradiated at 1.9 μm.[146]

The electrochemistry of numerous Tp*Mo(NO)XY complexes has been studied in considerable detail. The common starting material itself, Tp*Mo(NO)I_2, is reversibly reduced to a monoanion. This loses iodide ion, to form the solvated species, Tp*Mo(NO)I(solvent), which undergoes a reversible one-electron oxidation process.[147] Other simple complexes, Tp*Mo(NO)X_2 (X = NCS, N_3) were shown to undergo one-electron reductions at −0.13 V (for X = N_3) and at −1.64 V (for X = NCS).[148] Similar reduction potentials were also observed for complexes Tp*Mo(NO)I(OC_6H_4-$COOC_{12}H_{25}$), Tp*Mo(NO)Cl(NHC_6H_4-$C_{10}H_{21}$), and Tp*Mo(NO)(NHC_6H_4-$C_{10}H_{21}$)$_2$. Despite their low melting points, none of them exhibit liquid crystalline behavior.[149]

Cationic species, $[\mathrm{Tp^*Mo(NO)(A)_2}]^{2+}$, were prepared from Tp*Mo(NO)I_2 and a variety of heterocyclic amines (imidazole, *N*-methylimidazole, pyrazole, 3,5-dimethylpyrazole, and pyridine) and were isolated as their $[\mathrm{BPh_4}]^-$ salts. These paramagnetic complexes exhibit room-temperature EPR signals, with hyperfine coupling to Mo isotopes. They showed reversible one-electron reduction, but when A contained an NH proton, the reduction was irreversible.[150] Compounds Tp*Mo(NO)X(Z), where X = I or Cl and Z = alkoxy, aryloxy, or arylamido ligands, some of which contained bulky substituents, have been prepared and spectroscopically characterized. They underwent in electrochemical studies one-electron reduction processes, some of which were reversible. Complex Tp*Mo(NO)[O(CH_2)$_2$Br] was six-coordinate, as was shown by X-ray crystallography.[151]

Several types of monometallic complexes of general structure Tp*Mo(NO)Cl(YC_6H_4YH-*m*) were prepared, where Y was O or NH, as well as similar compounds based on the 1,5-disubstituted naphthalene skeleton. Bimetallic complexes were prepared from the above, by using the anion derived from the free YH (also including Y = S) group to displace chloride with Tp*Mo(NO)Cl_2. The monometallic species underwent a one-electron reduction, while the bimetallic complexes had two one-electron reductions. Interaction between the redox centers was weaker in bimetallic systems with Y = O, than in those with Y = NH.[152–154]

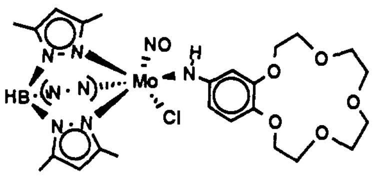
A series of para-substituted complexes of structure Tp*M(NO)Cl(NHC_6H_4Z-*p*) (M = Mo, Z = F, Cl, Br, OMe, SMe, CN, COOMe, NO_2) and (M = W, Z = Br, OMe, CN, COOMe, NO_2) was prepared and studied by cyclic voltammetry.[155] An analogous series, but containing meta-substituents, was also synthesized, characterized, and studied by cyclic voltammetry. There was a linear correlation between the reduction potentials within each series and the Hammett meta substituent parameters, σ_m, for Z.[156] Cyclic voltammetry studies were also carried out on compounds of the following general structures: Tp*M(NO)(X)(Y), including various combinations of M (Mo or W), X (I or Cl), and Y (OPh, SPh, NHPh, NC_4H_4), and Tp*Mo(NO)Y_2 (Y = OPh, SPh, NHPh, NC_4H_4). It was found that thiophenolate reduced at slightly more anodic potentials than their phenolate analogs, while the arylamide complexes reduced at significantly more cathodic potentials. Also, the tungsten complexes reduced at potentials about 0.45 V more cathodic than their molybdenum counterparts.[157] Complexes Tp*Mo(NO)Cl(Y), where M was Mo or W and Y were the anions of azetidine, pyrrolidine, and piperidine, all exhibited reversible one-electron reduction processes. The structure of a piperazine-bridged dinuclear complex **65** was determined by X-ray crystallography. It was a "strongly interacting" redox system with two one-electron reduction processes, separated by 560 mV.[158] Dinuclear complexes, Tp*Mo(NO)Cl(L–L)Tp*Mo(NO)Cl, and mononuclear ones, of structure Tp*Mo(NO)Cl(L–L), where L–L was 4,4'-bipyridyl, 3,3'-bipyridyl, *trans*-4,4'-dipyridylethylene, and 1,2-bis(4,4'-dipyridyl)ethane, were prepared and studied by EPR and electrochemical methods. The unpaired electrons in the dinuclear complexes show large interactions at 300 K.[159]



65

In a study of the bimetallic complex Tp*Mo(NO)I(NH-4-ferrocenylphenyl) it was shown that presence of an electron-rich group (such as $-NHC_6H_4-$) in the ligand bridging two metallic complexes prevents the transmission of electronic effects.[160] Another ferrocene-containing complex was prepared from Tp*Mo(NO)I_2 and 1,1'-dimercaptoferrocene. Its structure was determined by X-ray crystallography. The molecule has the usual chelated structure derived from the cyclic dimercapto ligand, and the ferrocenyl group is positioned so as to distance itself from Tp* (Fe–Mo distance 4.147(2) Å), being tilted toward the NO group. Electrochemical studies indicate an anomalously cathodic oxidation potential for the metallocene redox center.[161]

A number of novel, redox-responsive, molybdenum complexes have been prepared, which contain cyclic polyether cation coordinating sites. They are exemplified by **66** and **67**. The binding of sodium ions to the polyether sites shifts the reduction potential anodically by up to 320 mV.[162] The magnitude of the shift is relatively insensitive to the size of the cyclic polyether, but is significantly reduced when K^+ is used instead of Na^+.[163] At the same time, sodium ions tend to destabilize the complex. A more detailed study of alkali metal (Li^+, Na^+, K^+) complexing to the various cyclic ethers derivatives of the Tp*Mo(NO) moiety was carried out, and the structure of yet another cyclic ether derivative, Tp*Mo(NO)[*O*-$CH_2(CH_2OCH_2)_3CH_2O$], was determined by X-ray crystallography.[164] A different, though related, series of complexes was synthesized, where the Tp*Mo(NO)(Cl)-E redox center was linked through the heteroatom E (E = *p*-O, *m*-O, *o*-O, *p*-NH) to one of the phenyl groups in 5,10,15,20-tetraphenylporphyrin. Picosecond laser spectroscopy measurements on these complexes indicated that the observed fluorescence quenching is due to fast (τ < 30 ps) intramolecular charge separation, producing transient species with 120–290-ps lifetimes.[165] The area of redox-active bimetallic complexes has been reviewed.[166,167]



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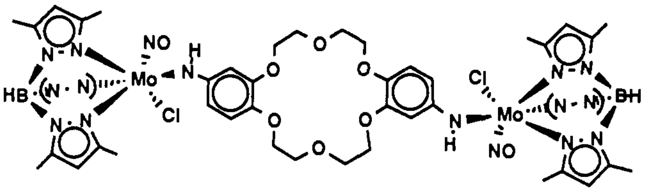

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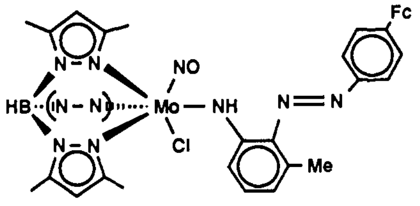
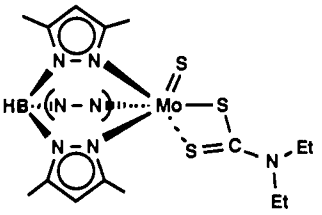
The compound **68** (Fc = ferrocenyl) was one of several related complexes, each containing a Tp*Mo(NO)(X) or Tp*W(NO)(X) moiety linked through diarylazo linkage to a ferrocenyl center, which were synthesized. Several of them have exhibited nonlinear optical properties, and their structures were determined by X-ray crystallography.[168,169]



68

While the extensive work reported above dealt with lower oxidation states of Mo, another large area of research was concerned with high oxidation states: Mo(IV), Mo(V), and Mo(VI), including oxomolybdenum and thiomolybdenum species. This was largely part of the quest for simple analogs of various molybdenum enzymes that are involved in nitrogen, sulfur or carbon metabolism. These include sulfite oxidase, nitrate reductase, xanthine oxidase, xanthine dehydrogenase, and aldehyde oxidase.[170,171] Again, the workhorse was the ligand Tp*, and the complexes used were often elaborated starting with the $[Tp^*Mo(CO)_3]^-$ anion.

The ^{95}Mo NMR was used extensively in complex characterization, and the ^{95}Mo spectra of $Tp^*Mo(NO)_2(Cl)$[172] and Tp*MoO(SS) (SS = R_2NCS_2, R = Me, Et, Pr; SS = $(EtO)_2PS_2$)[173] were compared with those of related compounds. The ^{95}Mo and ^{14}N NMR data were obtained and compared for a series of Tp*Mo(NO)XY complexes.[174] The complex Tp^*MoSCl_2, was the first mononuclear molybdenum(V) complex with a terminal sulfido ligand.[175] Numerous mononuclear oxo- and sulfidomolybdenum(IV) complexes were synthesized and studied by cyclic voltammetry, by NMR, and the structures of $Tp^*MoE(Et_2NCS_2)$ (E = O, S) were determined. In the complex **69** the coordination is octahedral, with bidentate dithiocarbamate ligand. The analogous oxo complex has a very similar structure.[176,177] However, in the Mo(III) complexes represented by **70**, which are prepared by the reaction of $[Tp^*Mo(CO)_3]^-$ with tetraalkylthiuram disulfides, only one dithiocarbamate ligand is bidentate, the second one is monodentate.[178,179] The reaction of $[Tp^*W(CO)_3]^-$ with tetraalkylthiuram disulfide yields the tungsten analog of **69**.[180]



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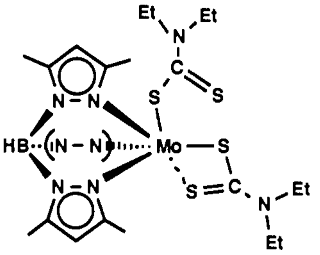

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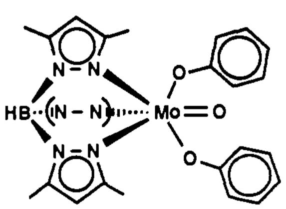
The structure of octahedral Mo(V) complex $Tp^*MoO(OPh)_2$ (**71**) was determined by X-ray crystallography,[181] as was that of the related $Tp^*MoO(OC_6H_4\text{-}p\text{-}Cl)_2$ analog.[182] The structures of these complexes are very similar to those of $Tp^*MoO(NCS)_2$, and $Tp^*MoO(N_3)_2$,[183] and essentially identical to that of the phenylthio analog $Tp^*MoO(SPh)_2$, which was prepared,



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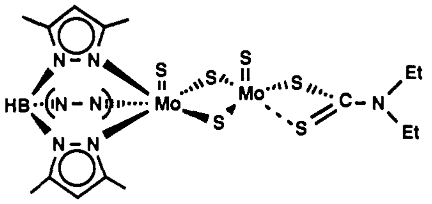
along with a large number of oxomolybdenum(V) complexes of general composition Tp*MoOXY (X, Y = Cl, NCS, N_3, OR, SR). Also synthesized were chelated structures, where XY was derived from the dianions of ethylene glycol, 2-mercaptoethanol, 1,2-ethanedithiol, catechol, *o*-mercaptophenol, *o*-aminophenol, *o*-aminobenzenethiol, and toluenedithiol. These compounds were characterized by EPR, cyclic voltammetry, UV–visible spectroscopy, and mass spectrometry.[184] Complexes Tp*MoO(diolato) and Tp*MoO(dithiolato), involving five-, six-, and seven-membered rings, were synthesized and fully characterized. Charge-transfer character was observed in the lowest energy electronic absorptions for the dithiolato complexes, but not for the diolato ones. Both series show decreases in the Mo(V)/Mo(IV) reduction potential with increasing chelate ring size (0.12–0.22 V per additional methylene).[185] The He I valence photoelectron spectra of these compounds were also studied.[186] The EPR spectra and electronic structures of some of the nonchelated Tp^*MoOX_2 complexes were measured and calculated on the basis of C_s symmetry for the molecules.[187] ESR studies were also done on Tp^*MoOCl_2, diluted with the pseudoisostructural chlorotin(IV) moiety.[188] The spectra at the molybdenum L_2 and L_3 edges have been recorded and analyzed for an extended series of Tp*MoOXY complexes, looking for similarity to the spectra of enzymes such as, for instance, sulfite oxidase.[189]

The three novel polynuclear oxo- and sulfidomolybdenum complexes, **72–74**, were synthesized and structurally characterized by X-ray crystallography.[190] Another dinuclear complex, $[Tp^*MoO_2(OC_6H_4\text{-}o\text{-}S)]_2$, containing Mo(VI), was obtained from recrystallization in air of the complex $Tp^*MoO_2(OC_6H_4\text{-}o\text{-}S)$. The dimer is linked via a disulfide bond, and its structure was established by X-ray crystallography.[191]



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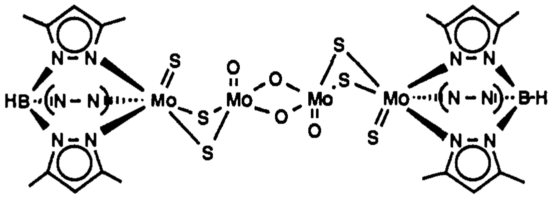

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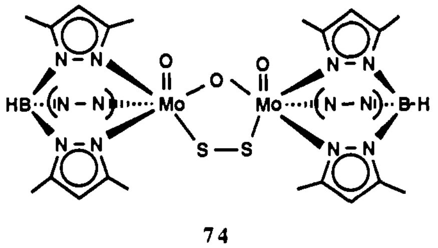
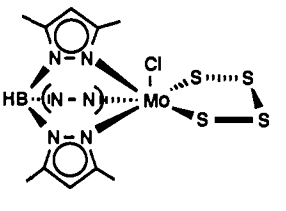


74

The family of stable complexes $Tp^*MoX(S_4)$ (X = F, Cl, Br, NCS) was synthesized by treating the appropriate Tp^*MoO_2X precursors with boron sulfide. The structure of Tp^*MoClS_4 (**75**), was established by X-ray crystallography. It shows distorted octahedral coordination, and the Mo–S bonds are remarkably short (2.192 Å).[192] Reaction of $Tp^*Mo(S_4)(NCS)$ with dimethyl acetylenedicarboxylate yields the product **76**, in which the two outer sulfur atoms have been replaced by the dicarbomethoxyvinylidene moiety.[193]



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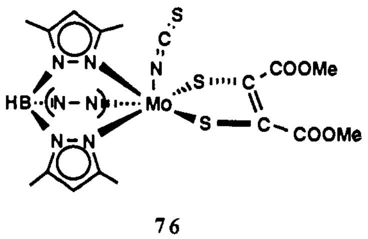

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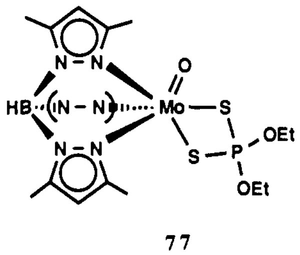
The direct reaction of $Mo_2O_3[(EtO)_2PS_2]_4$ with Tp*K, improved by the presence of PPh_3, yields two products: **77**, in which the $(EtO)_2PS_2$ ligand is bidentate, and the Mo(VI) analog, **78**, which contains monodentate $(EtO)_2PS_2$ ligand, with the second sulfur remote from the metal, as was established by X-ray crystallography.[194] An interesting mixed-valence binuclear complex, containing Mo(V) and Mo(VI) was obtained as one of the products from the reaction of Tp^*MoO_2Cl with a variety of Grignard reagents. Its structure, **79**, was determined by X-ray crystallography.[195] The oxygen-transfer activity of several representatives from the Mo(VI) family Tp^*MoO_2X (X = F, Cl, Br, NCS, OPh, OMe, SPh), has been tested with Ph_3P. It resulted in formation of Ph_3PO and the coordinatively unsaturated Tp*Mo(O)X. This complex became solvated in donor solvents, it abstracted a Cl atom from methylene chloride, and it formed in toluene the Mo(V) dimer, $[Tp^*MoOCl]_2O$.[196]



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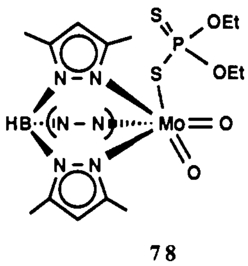

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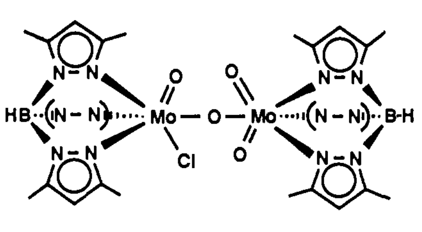
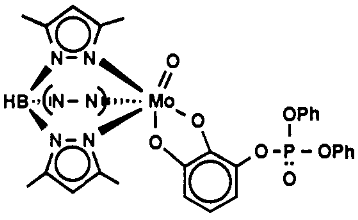


79

In the search for models simulating the molybdenum–phosphate interactions in "oxo-type" molybdoenzymes and their cofactors, several types of Tp* derivatives were prepared, containing a phosphate functionality in the molecule, as in **80** (and its meta analog), and



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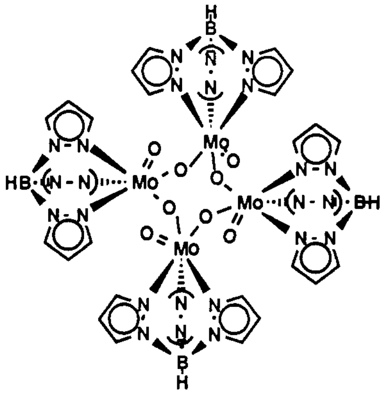
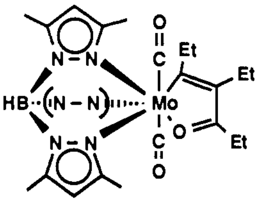
their ^{31}P NMR spectra were studied. They were the first examples of ^{31}P NMR resonance broadening in oxomolybdenum(V) centers within discrete molecules. Other types of phosphate derivatives were obtained by treatment of Tp^*MoO_2Cl with resorcinol or hydroquinone in 1:1 ratio, followed by phosphorylation of the resulting intermediates with $(PhO)_2POCl$. The products, $Tp^*MoO_2[OC_6H_4\text{-}p\text{-}OPO(OPh)_2]$ and its meta analog, were characterized by ^{31}P NMR. The nonbonding Mo–P distance is in the 4–8-Å range.[197,198]

Various Tp-based oxomolybdenum species were also studied. A very clean route to $[TpMoO_3]^-$ was found, based on the reaction of $[TpMo(CO)_3]^-$ with dimethyldioxirane. Two byproducts are obtained: one is the dinuclear $[TpMoO_2]_2(\mu\text{-}O)_2$ and the other is an unusual monocyclic oxomolybdenum(V) tetramer (**81**), the structure of which was determined by X-ray crystallography.[199] Additional oxomolybdenum Tp derivatives, structurally characterized by X-ray crystallography, were $TpMoOCl_2$ and $[TpMoOCl]_2O$, which was isolated as two geometric isomers, and the structurally rather complex $[Tp_2Mo_4(O)_4(\mu\text{-}O)_4(\mu\text{-}OMe)_2(MeOH)_2]$. The $[TpMoOCl]_2O$ dimers differed in their symmetry: one had an approximate C_2 axis, while the other, which was the major product, had a crystallographically imposed center of symmetry.[200] Detailed studies of the electronic and vibrational spectroscopy of the above oxymolybdenum complexes permitted assignment of the various characteristic bands in their infrared and Raman spectra.[201] Other examples, where a Tp ligand is bonded to coordination sites in Mo clusters are the compounds $Tp_4(Mo_4S_4)pz$, where two Tp ligands are tridentate, two Tp ligands are bidentate, and the pz group bridges the Mo centers bonded to η^2-Tp groups.[202] Another related cluster, $[Tp_2Mo_3S_4](\mu\text{-}O)(\mu\text{-}pz)_2$, contains tridentate Tp ligands, with the (μ-O) and two (μ-pz) units acting as bridges between the two Mo_3 subunits.[203] The structure of a complicated trinuclear cluster, based on two $TpMo(CO)_2$ carbyne units, containing a Mo–Pt–Mo sequence, and in addition, involving a ferrocene moiety, was determined by X-ray crystallography.[204]



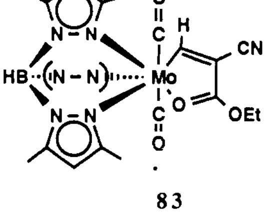
81

Deprotonation of the $Tp^*Mo(CO)_2(\eta^2\text{-}COCH_3)$ or of $Tp^*Mo(CO)[P(OPh)_3](\eta^2\text{-}COCH_3)$ with BuLi or KH yields the corresponding enolates, which can be alkylated at the carbon with reactive alkyl halides (MeI, $PhCH_2Br$). $Tp^*Mo(CO)_2(\eta^2\text{-}COCMe_3)$ was prepared in this fashion. The structure of $Tp^*Mo(CO)[P(OPh)_3](\eta^2\text{-}COCHMePh)$ was determined by X-ray crystallography.[205] Further work with the above enolates led to additional phosphite complexes, $Tp^*Mo(CO)[P(OPR)_3](\eta^2\text{-}COR')$; strong bases generate the reactive enolates, e.g. $Tp^*Mo(CO)[P(OPR)_3](C(O)C{=}CHR')$, which react stereoselectively with benzyl bromide. They also condense with benzaldehyde or benzophenone, yielding unsaturated η^2-enone complexes, which undergo conjugate additions leading to saturated η^2-acyl products. Heating generates η^3-complexes, while insertion of alkynes into the C–Mo bond under carbon monoxide forms oxametallacycles, exemplified by **82**, the structure of which was determined by X-ray crystallography. The rotational preference of the enolates was probed with EHMO calculations.[206] Treatment of $Tp^*Mo(CO)_2(\eta^2\text{-}COR)$, where R = Me, Et, with excess NaOEt affords carbyne complexes, $Tp^*Mo(CO)_2({\equiv}CR)$. These can be deprotonated at low temperatures to yield anionic vinylidene complexes, which react with alkyl halides at the vinylidene β-carbon. A η^2-ketenyl complex is produced by the addition of CO to the phenylcarbyne derivative.[207]



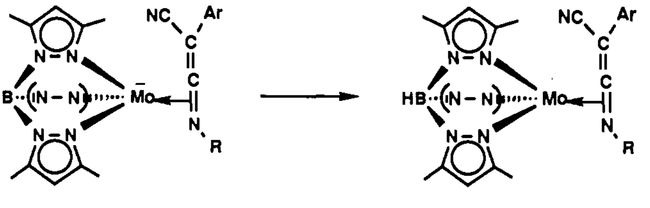
82

The chlorocarbyne, $Tp^*Mo(CO)_2{\equiv}CCl$, is an excellent starting material for a variety of derivatives, through displacement of the carbyne chloride by nucleophiles. The anions derived from active hydrogen compounds, such as YCH_2Z (Y, Z = CN, COOR) react readily, forming $[Tp^*Mo(CO)_2{\equiv}CCHYZ]^-$ complexes, which can be deprotonated and isolated as quaternary ammonium salts. These have been converted to the metallacycle **83**, the structure of which was established by X-ray crystallography, or to its analogs, and also to derivatives such as $Tp^*Mo(CO)_2{\equiv}CC(YZX)$, where X was HgCl, HgBr, HgI, Cu, or $N{=}NC_6H_4NMe_2$.[208] The



83

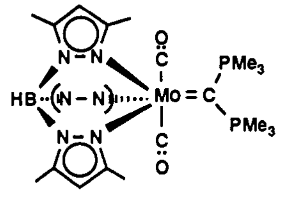
metal derivatives containing the cationic fragment, such as HgCl, have a structure in which the metal is coordinated to both the triple bond of the carbyne and also to the ester carbonyl. Reaction of [Tp*Mo$(CO)_2{\equiv}CCYZ]^-$ with RN_3 yielded the anion 84, which was converted to the air-stable 17-electron radical 85, the structure of which was established by X-ray crystallography, as was the structure of the aroylcarbyne Tp*Mo≡CC(O)Ar, obtained from [Tp*Mo$(CO)_2{\equiv}CCYZ]^-$ via oxidative hydrolysis.[209] The anion



84 85

$[CpFe(CO)_2]^-$ reacted with Tp*Mo$(CO)_2{\equiv}CCl$, yielding the dinuclear complex Tp*Mo$(CO)_2{\equiv}CFeCp(CO)_2$, which was structurally characterized by X-ray crystallography.[210]

The carbyne chemistry was studied to an even greater extent in the tungsten system. Displacement of chloride in Tp*M$(CO)_2{\equiv}CCl$ complexes (M = Mo, W) with aryloxide ions produced the aryloxy carbyne derivatives, Tp*M$(CO)_2{\equiv}C(OAr)$, while tertiary phosphines gave cationic species [Tp*M$(CO)_2{\equiv}C(PR_3)]^+$. They were characterized by ^1H and ^{13}C NMR, and the structure of [Tp*W$(CO)_2{\equiv}C(PMe_2Ph)][PF_6]$ was determined by X-ray crystallography.[211] The diphosphonium carbene cation, [Tp*M$(CO)_2{=}C(PMe_3)_2]^+$, was prepared by the addition of PMe_3 to the cation [Tp*M$(CO)_2C(PMe_3)]^+$, and its structure, as the PF_6^- salt, is as shown in 86. Reaction with methyl iodide regenerates the starting cation.[212] The plain carbynes of Mo and W were prepared by desilylation of the Tp*M$(CO)_2{\equiv}C(SiCMe_2Ph)$ complexes with Bu_4NF. While the carbyne Tp*W$(CO)_2{\equiv}CH$ is stable and was fully characterized spectroscopically and by osmometric molecular weight determination, the Mo analog dimerized to a vinylidene-bridged complex, 87, the structure of which was determined by X-ray crystallography.[213]



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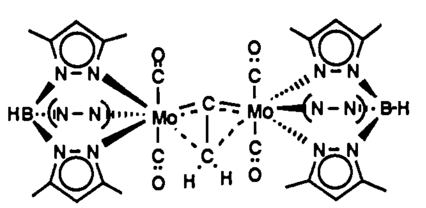
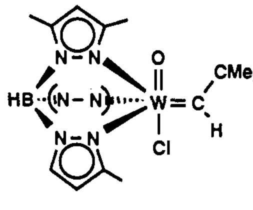
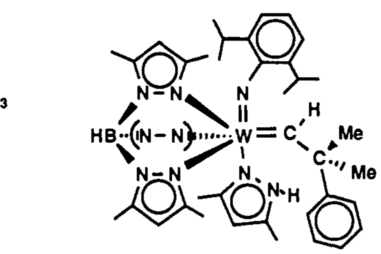


87

Tp*W$({\equiv}CBu^t)Cl_2$, an exceptionally stable (thermally, oxidatively, and hydrolytically) complex, was converted to Tp*W$({=}C(H)Bu^t)(O)Cl$ (88), the structure of which was determined by X-ray crystallography. In the presence of 1 equiv of $AlCl_3$, 88 catalyzed readily ring opening polymerization of cyclooctene, or of norbornene, to a high polymer even in the presence of air. The active catalytic species is thought to involve a five-coordinate cationic alkylidene.[214] Related complexes exemplified by the cation 89 (with CF_3SO_3 anion) were prepared from KTp or KTp* and $W({=}CHCMe_2Ph)({=}NAr)(OTf)_2(DME)$. Complex 89, the structure of which was determined by X-ray crystallography, can be deprotonated with nBuLi and reprotonated back to 89 with triflic acid. The 89 analog contained coordinated CF_3SO_3 instead of 3,5-Me_2pzH. Rotational isomers of these complexes were studied by ^1H NMR. These complexes were inert toward cyclooctene by themselves, but in the presence of $AlCl_3$ caused rapid ring-opening polymerization.[215]

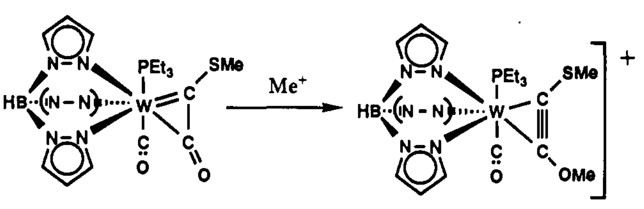


88

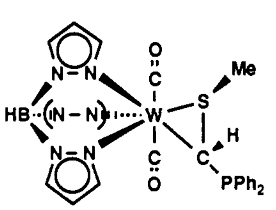


89

The (methylthio)carbyne, TpW$(CO)_2{\equiv}C(SMe)$, yielded with PEt_3 the η^2-ketenyl derivative 90, which was methylated at the ketenyl oxygen to produce the cationic complex 91, while protonation of the carbyne yields the cationic carbene complex, [TpW$(CO)_2(\eta^2$-CHSMe$)]^+$, which readily adds phosphine ligands and forms cations [TpW$(CO)_2(\eta^2$-CHSMe$)(PR_3)]^+$. The cationic complex [TpW$(CO)_2(\eta^2$-CHSMe$)(PPh_2H)]^+$ can be deprotonated, yielding [TpW$(CO)_2(\eta^2$-CHSMe$)(PPh_2)]$, whose structure, 92, was established by an X-ray diffraction study.[216] Addition of nucleophiles,



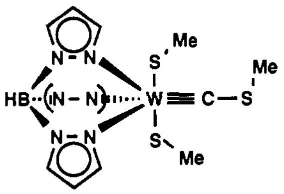
90 91



92

such as the anions of mercaptans or of ethylene malonate, to the carbene carbon in [TpW$(CO)_2(\eta^2$-CHSMe$)]^+$ gives rise to complexes [TpW$(CO)_2(\eta^2$-CHSMe$)X]$, where X is SMe, SEt, SPr^i, or $CH(COOMe)_2$, and 4-(dimethylamino)pyridine yields the stable cation [TpW$(CO)_2(\eta^2$-CHSMe$)(4$-Me_2Npyridine$)]^+$. However, with secondary amines the reaction takes a different course and (dialkylamino)carbyne complexes, [TpW$(CO)_2{\equiv}CNR_2]$ are formed

(R = Me, Et). Primary amines, RNH_2 (R = Me, Et, iPr, tBu, CH_2CH_2OH, *p*-tolyl) yield the corresponding aminocarbynes $TpW(CO)_2{\equiv}CNHR$, but they are in equilibrium with $[TpW(CO)_2(H)(CNR)]$, which are their hydride–isocyanide tautomers. Still other bases deprotonate $[TpW(CO)_2(\eta^2\text{-}CHSMe)]^+$ with regeneration of the original (alkylthio)carbyne.[217] The thiocarbyne $TpW(CO)_2{\equiv}CSMe$ reacts with the electrophile MeS^+ to yield the cation $[TpW(CO)_2(\eta^2\text{-}C(SMe)SMe)]^+$. It can act as a MeS^+ transfer agent, and it also reacts with nucleophiles, X^-, forming $TpW(CO)_2(\eta^2\text{-}C(SMe)(X)SMe)]$ (X = SR, H, Me, PMe_3).[218] Thermolysis of $[TpW(CO)_2(\eta^2\text{-}C(SMe)(SR)SMe)]$ results in CO loss, C–S bond cleavage, and RS migration, yielding new carbynes, exemplified by $TpW(SMe)(SR){\equiv}CSR'$. By contrast, complexes $[TpW(CO)_2(\eta^2\text{-}C(SMe)(SAr)SMe)]$ eliminate ArSSMe, producing the known carbyne $TpW(CO)_2{\equiv}CSMe$. At the same time, upon photolysis, complexes $[TpW(CO)_2(\eta^2\text{-}C(SMe)(SAr)SMe)]$ are converted to carbynes similar to **93**.[219]



93

Coordinated acetonitrile in $[Tp^*W(CO)(1\text{-phenylpropyne})(MeCN)BF_4$ was reduced stepwise by sequential treatment with Et_3BHLi, followed by HBF_4. Complexes representing each of the hydrogen-addition stages, up to ethylamine, were isolated and characterized.[220,221] An unusual tungsten(IV) complex, containing both a carbonyl ligand and an oxo group was synthesized by the reaction of $Tp^*W(CO)_3X$ (X = Br or I) with molecular oxygen, which yields $Tp^*W(CO)(O)X$, the octahedral structure of which was determined by X-ray crystallography.[222] Complexes $Tp^*W(CO)_2NHR$, which are obtained from $Tp^*W(CO)_3I$ and RNH_2, were converted by iodine to cationic nitrene monomers, $[Tp^*W(CO)_2(\eta^2\text{-}NR)]^+$. The octahedral structures for these complexes (R = tBu and R = Ph) were established by X-ray crystallography.[223]

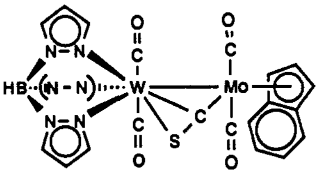
Protonation of the anion $[Tp^*W(CO)_3]^-$, prepared from Tp*K and $W(CO)_6$, gave the W–H derivative, $[Tp^*W(CO)_3]H$, the structure of which shows octahedrally coordinated W and only a single type of pz* in the NMR. The $^{183}W\text{–}^1H$ coupling is small (6 Hz), and the W–H appears at −2.42 ppm. By contrast, the structurally characterized complex $[Tp^*W(CO)_3(1\text{-phenylpropyne})H]$, which was prepared by replacement of acetonitrile from a cationic precursor with hydride ion, had the W–H at 9.80 ppm and $^{183}W\text{–}^1H$ coupling of 116 Hz.[24] Oxidative hydrolysis of $[Tp^*W(CO)_3]^-$ produces the structurally characterized mixed-valence oxocarbonyl complex $Tp^*W^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)Tp^*$.[224]

A β-agostic methylphenylcarbene complex, $Tp^*W(CO)_2{=}CMe(Ph)$, was obtained after sequentially treating the $[Tp^*W(CO)_2(\text{phenylacetylene})]^+$ first with $LiHBE_4$, then with MeLi, and finally, with HBF_4. The agostic bonding was suggested by NMR data and was compatible with the structure determined by X-ray crystallography. This type of chemistry was elaborated in greater detail, and applied to cationic bis-alkyne complexes $[Tp^*W(CO)(PhC_2H)(PhC_2R)]^+$, in which the two alkyne ligands donate a total of six electrons, as was indicated by NMR and crystal data for the bisphenylacetylene structure. This species yields upon deprotonation the alkyne acetylide complex, $Tp^*W(CO)(PhC_2H)(C_2Ph)$, which exists as two isomers in solution.[225,226] A series of complexes $Tp^*W(CO)(I)(RC_2R')$ and $[Tp^*W(CO)(L)(PhC_2Ph)][BF_4]$ has been synthesized and studied spectroscopically and by X-ray crystallography for complexes $[Tp^*W(CO)(MeCN)(RC_2R')][BF_4]$ and $Tp^*W(CO)(I)(PhC_2Me)$.[227]

The reaction of $[Tp^*W(CO)_2(NPh)][PF_6]$ with $LiBH_4$ yields the complex $Tp^*W(CO)(NPh)(CHO)$ which undergoes intramolecular hydride migration from carbon to nitrogen, forming $Tp^*W(CO)_2(NHPh)$. The metal formyl intermediate is fluxional, with the hydride migrating between the formyl and carbonyl groups; rate constants for this degenerate process have been determined.[228] Trimethyl phosphite reacts with $[Tp^*W(CO)_2(PhC{\equiv}CH)][BF_4]$, readily forming the η^2-complex $Tp^*W(CO)_2[\eta^2\text{-}CPh{=}CHP(O)(OMe)_2]$ which can be protonated at the oxygen, to yield the cationic species $[Tp^*W(CO)_2[\eta^2\text{—}CPh{=}CHP(OH)(OMe)_2]][BF_4]$. The $[Tp^*W(CO)_2(PhC{\equiv}CMe)][BF_4]$ salt reacts with $LiBEt_3H$ forming a η^2-intermediate, which transforms into η^3-allyl complexes, while with $LiCu(Bu^n)_2$, the η^2-acyl complex is formed, in which the alkyne ligand acts as a four-electron donor.[229] A reactive propargyl anion is prepared by the deprotonation of $Tp^*(CO)(I)(PhC{\equiv}CCH_3)$, which reacts with reactive halides, such as MeI or $PhCH_2Br$, yielding an appropriately substituted alkyne. Deprotonation of $Tp^*(CO)(I)(PhC{\equiv}CCH_2CH_3)$, followed by benzylation produces a single diastereomer as determined by ^1H NMR, while methylation of the anion formed from $Tp^*(CO)(I)(PhC{\equiv}CCH_2Ph)$ produces the opposite diastereomer. Benzaldehyde adds to the coordinated η^2-propargyl carbanion, $[Tp^*W(CO)(I)(\eta^2\text{-}PhC{=}C{=}CHMe)]Li$, forming $Tp^*W(CO)(I)(PhC{\equiv}CHMeCH(OH)Ph)$, the structure of which was determined by X-ray crystallography. A coordinated enyne was obtained from the benzaldehyde adduct, by first forming the mesyl derivative and then eliminating $MeSO_3H$ to yield the complex $Tp^*W(CO)(I)(PhC{\equiv}CCMe{=}CHPh)$.[230]

The reaction of Tp^*WO_2Cl with a variety of Grignard reagents produced octahedral organometallic dioxo–W^{VI} complexes Tp^*WO_2R (R = Me, Et, Ph, CH_2Ph), stable toward β-elimination. This reaction does not work with Tp^*MoO_2Cl. The structures of complexes with R = Et and R = Ph were established by X-ray crystallography. Complexes Tp^*WOSCl and Tp^*WS_2Cl were obtained from Tp^*WO_2Cl and B_2S_3.[231,232]

Heterobinuclear complexes $TpW(CO)_2(CS)\text{–}Au(PR_3)$ were prepared from $[TpW(CO)_2(CS)]^-$ and $ClAu(PR_3)$, containing semibridging CS and one semibridging CO. This was the first example of a semibridging CS ligand, which showed stronger bonding to Au than did CO. The structure of $TpW(CO)_2(CS)\text{–}Au(PMe_3)$ was determined by X-ray crystallography.[233] The CS ligand was found to be side-on bridging and donating four electrons in the structurally characterized complex **94**.[234] The regioselective addition of Pt–H or Pt–R bonds across alkylidyne M–C triple bonds affords cationic heterobinuclear complexes, containing μ-alkylidene ligands in one step. A number of examples of this reaction have been reported, and the structure of **95** was determined by X-ray crystallography.[235]



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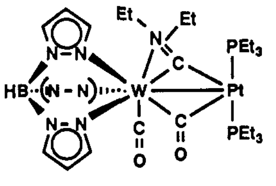
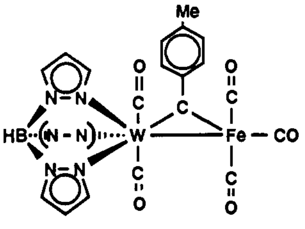


95

Partial oxidative decarbonylation of $[\mathrm{Tp^*W(CO)_3}]^-$ with thiuram disulfide yielded, en route to $\mathrm{Tp^*WS(S_2CNEt_2)}$, two intermediate products, which were isolated and characterized: $\mathrm{Tp^*W(CO)_2(S_2CNEt_2)}$, which had seven-coordinate W, and the unusual mixed-valence complex $\mathrm{Tp^*W^{II}(CO)_2(\mu\text{-}S)W^{IV}(S_2CNEt_2)_2(S_2CNEt_2)}$.[236]

The ligands Tp and, and to a lesser extent pzTp, have also found wide use in capping three coordination sites of various homo- and heteropolymetallic clusters and related species of Mo and W. Thus, $\mathrm{TpW(CO)_2{\equiv}CR}$ reacted with $\mathrm{Fe_2(CO)_9}$ to yield the structurally characterized $\mathrm{TpW(CO)_2(\mu\text{-}CR)[Fe(CO)_3]}$, which also contains a W–Fe bond.[237] Similarly, compounds such as $\mathrm{[TpWRh(\mu\text{-}CMe)(CO)_2(PPh_3)_2][PF_6]}$, $\mathrm{[TpWRh(\mu\text{-}CMe)(CO)_2(COD)][BF_4]}$, and related complexes, were prepared from $\mathrm{TpW(CO)_2{\equiv}CR}$ and the appropriate Rh precursors.[238] Dinuclear and trinuclear W–Rh complexes, the latter of structure $\mathrm{TpW(CO)_2(\mu\text{-}CO)(\mu_3\text{-}CSMe)(RhL)_2}$, which contains a triangle of $\mathrm{Rh_2W}$ atoms, were synthesized, as was the trinuclear $\mathrm{TpW(CO)_2(\mu_3\text{-}CSMe)(NiCp)_2}$.[239] Structures of the starting carbyne $\mathrm{pzTpW(CO)_2({\equiv}C\text{-}}p\mathrm{\text{-}tolyl)}$, of the above $\mathrm{Rh_2W}$ complex and of a related FeRhW cluster with the same triangular array of metal atoms were established by X-ray crystallography.[240] A large number of dinuclear and trinuclear Fe–W and $\mathrm{Fe_2}$–W similar to those above were prepared, and the structures of **96** and **97** were established by X-ray crystallography.[241]



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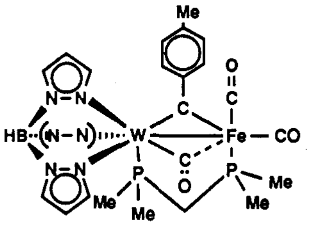
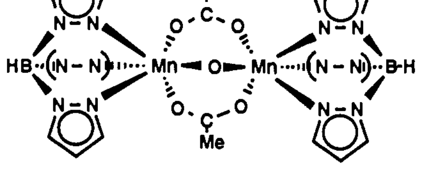


97

Transformations of complex **96**, and of related ones, upon reaction with phosphines and with other reactants were studied, and the structure of one of the products, $\mathrm{TpW(CO)_2(\mu\text{-}PPh_2)[(Fe(CO)_3]}$, which contains a W-Fe-P triangle, was established by X-ray crystallography.[242] Also synthesized were complexes containing a linear array of W–Pt–W, exemplified by the structurally characterized $\mathrm{[TpW(CO)(\mu\text{-}CO)(\mu\text{-}CR)]_2Pt}$. Other linear trinuclear complexes of this type included W–Ni–W, Mo–Pt–Mo, W–Au–W arrays, and the rare Cr–Pt–Cr complex. Also prepared were dinuclear, metal–metal bonded complexes $\mathrm{TpM(CO)_2({\equiv}CR)Pt(PR_3)_2}$ where M = Cr, Mo, W.[243] Other triangular trimetallic complexes included those containing $\mathrm{WMo_2}$ and $\mathrm{MoW_2}$ clusters. Further examples consisted of several binuclear Mo–Fe complexes.[244] The tetranuclear cluster $\mathrm{TpW(\mu_3\text{-}CR)Ru_3(CO)_{11}}$ was prepared in good yield from $\mathrm{TpW(CO_2\text{-}(\eta^3\text{-}CR)}$ and excess of $\mathrm{Ru(CO)_4(\eta\text{-}C_2H_4)}$.[245] Also reported was the dinuclear complex $\mathrm{[TpCrMo\{\mu\text{-}\sigma{:}\eta^6\text{-}CC_6H_4\text{-}(OMe\text{-}2)\}(CO)_5}$.[246] Structurally related complexes, $\mathrm{TpMo(CO)_2({\equiv}CC{\equiv}CBu^t)}$, $\mathrm{TpMW(CO)_2({\equiv}CC{\equiv}CBu^t)}$, and $\mathrm{Tp^*Mo(CO)_2({\equiv}CC{\equiv}CBu^t)}$ were prepared in good yield. Upon reaction with $\mathrm{Co_2(CO)_8}$, complexes $\mathrm{Tp^*Mo(CO)_2(\mu_3\text{-}CC{\equiv}CBu^t)[Co_2(CO)_6]}$ and $\mathrm{TpW(CO)_2(\mu_3\text{-}CC{\equiv}CBu^t)[Co_2(CO)_6]}$, were formed, along with related compounds.[247]

6. Group VIIB: Mn, Tc, Re

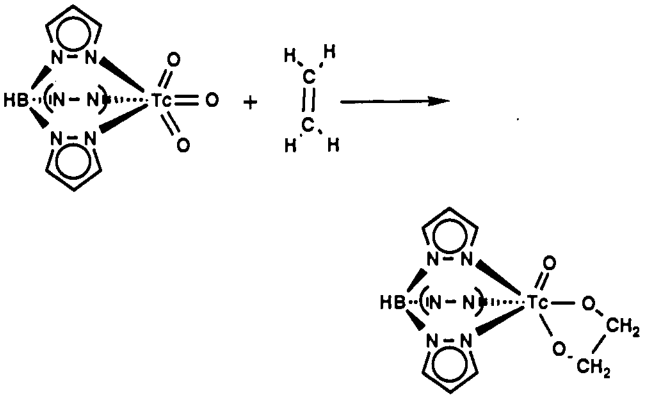
Several dinuclear dimanganese(III) complexes, $\mathrm{TpMn(\mu\text{-}O)(\mu\text{-}OOCR)_2MnTp}$, were synthesized (R = H, Me, or Et) in a quest for model compounds that might mimic the properties of known binuclear manganese enzymes. These were studied by cyclic voltammetry, and the structure of **98** was determined by X-ray crystallography.[248] The dinuclear complex $\mathrm{TpMn(\mu\text{-}O)(\mu\text{-}OAc)_2MnTp}$ was studied by X-band EPR spectroscopy.[249] A high-potential mononuclear Mn(IV) complex $\mathrm{[Tp^*_2Mn]^{2+}}$ was synthesized by oxidation of $\mathrm{[Tp^*_2Mn]}$ with $\mathrm{KMnO_4}$ and isolated as the diperchlorate salt, the structure of which was determined by X-ray crystallography. This complex was studied by EPR and cyclic voltammetry, showing the highest $\mathrm{Mn^{IV}/Mn^{III}}$ reduction potential in $\mathrm{Mn^{IV}}$ mononuclear complexes (1.35 V). The analogous $\mathrm{[Tp_2Mn]^{2+}}$ species was also prepared, but was difficult to purify.[250]



98

The first technetium complex containing a Tc=S bond, $\mathrm{TpTcSCl_2}$, was obtained by reacting $\mathrm{TpTcOCl_2}$ with $\mathrm{B_2S_3}$; the Re analog, $\mathrm{TpReSCl_2}$, was prepared similarly. These compounds were characterized by IR, mass spectrometry, and magnetic susceptibility measurements. They displayed parallel properties.[251] The dicarbonyltechnetium species, $\mathrm{TpTc(CO)_2(PPh_3)}$ was prepared in good yield and structurally characterized.[252]

High oxidation state technetium(VII) and rhenium(VII) complexes, $\mathrm{TpTcO_3}$ and $\mathrm{TpReO_3}$, were prepared by oxidation of $\mathrm{TpMOCl_2}$ with nitric acid and by other methods. $\mathrm{TpTcO_3}$ adds ethylene, forming the glycolate complex **99**. The corresponding Re complex is unstable with respect to $\mathrm{TpReO_3}$.[253] $\mathrm{TpReO_3}$ was also prepared from $\mathrm{Re_2O_7}$ and TpNa, and its structure was determined by X-ray crystallography.[254] $\mathrm{Tp^*ReO_3}$ was prepared similarly. It reacts with $\mathrm{PPh_3}$ in THF, in the presence of $\mathrm{Me_3SiCl}$, at room temperature to yield $\mathrm{Tp^*ReO(OH)Cl}$; at reflux, however, an inseparable mixture of $\mathrm{Tp^*ReO(OH)Cl}$ and $\mathrm{Tp^*ReOCl_2}$ is formed. The chloride ion in $\mathrm{Tp^*ReO(OH)Cl}$ has been replaced with anions of a series of aromatic thiophenols, yielding complexes $\mathrm{Tp^*ReO(OH)(SAr)}$. The heterobimetallic complex $\mathrm{Tp^*ReO(OH)SC_6H_4OMo(NO)ClTp^*}$ was obtained from the reaction of $\mathrm{Tp^*ReO(OH)(SC_6H_4OH)}$ and $\mathrm{Tp^*Mo(NO)Cl_2}$.[255] The reaction of ammonium perrhenate with Tp* resulteed in decomposition of the



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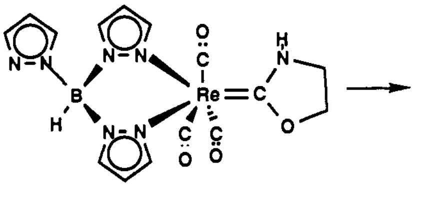
Tp* ligand, and the product isolated was [H3,5Me$_2$pz)$_2$ReO]$_2$O.[256] TpReO$_3$ is readily reduced by PPh$_3$, in the presence of excess Me$_3$SiX (X = Cl, Br), to yield Re(V) complexes TpReOX$_2$ (X = Cl, Br, pz). Thiophenol reacts with TpReOCl$_2$, depending on conditions, affording either TpReO(SPh)Cl or TpReO(SPh)$_2$. 1,2-Ethanedithiol and 1,2-benzenedithiol yield the corresponding chelated dithioethers, both of which were structurally characterized.[257] TpReOCl$_2$ reacts with LiAlH$_4$, yielding TpReH$_6$, which has a classical structure without direct H–H bonds, as was deduced from variable-temperature ^{1}H NMR T_1 data and isotope shifts of hydride resonances upon deuterium substitution.[258]

The carbonyl complex TpRe(CO)$_3$ upon irradiation in THF loses CO yielding the solvated species TpRe(CO)$_2$THF, from which THF was displaced by a variety of ligands: MeCN, pyridine, PMe$_2$Ph, PPh$_2$, or cyclohexyl isonitrile. Two of these octahedral complexes were structurally characterized. With Ph$_2$P(CH$_2$)$_3$PPh$_3$, two products were obtained: the singly substituted TpRe(CO)$_2$(L) and the dinuclear, bridged species [TpRe(CO)$_2$]$_2$[Ph$_2$P(CH$_2$)$_3$PPh$_3$].[259] The Tp complex **100**, in which Tp is bidentate, was prepared by bromide displacement from the appropriate precursor; the tridentate Tp complex **101** is obtained from the former upon irradiation and loss of one CO ligand.[260]



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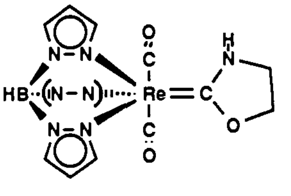

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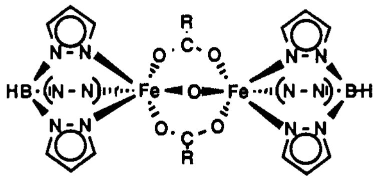
7. Group VIII: Fe, Ru, Os

Among the mononuclear iron complexes, the anionic complexes [TpFeCl$_3$]$^-$ and [Tp*FeCl$_3$]$^-$ were synthesized, in which the chloride was displaceable by, e.g., azide ion. Structures of [TpFeCl$_3$]$^-$ and of [Tp*Fe(N$_3$)$_3$]$^-$ were determined by X-ray crystallography.[261] The same anion [TpFeCl$_3$]$^-$ was prepared by a different method and isolated as the [Tp$_2$Fe]$^+$ salt, the structure of which was determined by X-ray crystallography, as was that of the binuclear complex TpFe(μ-O)(μ-O$_2$CCH$_3$)FeTp[262] and of [Tp$_2$Fe]$^+$[NO$_3$]$^-$.[263]

The octahedral Tp$_2$Fe was part of a study investigating spin-exchange processes in transition metal complexes,[264] partial molal volumes, and the concentration dependence of apparent molal volumes, in spin-equilibria complexes.[265] The spin equilibria in a set of related complexes: Tp$_2$Fe, pzTp$_2$Fe, Tp*$_2$Fe, and Tp$^{Me3}{}_2$Fe were studied by Mössbauer spectroscopy at low temperature and high pressure. The spin states were found to be susceptible to pressure, and the low- and high-spin states could be interchanged by applying appropriate pressures and temperatures.[266] The high-temperature spin-state crossover in Tp$_2$Fe was studied by IR and Mössbauer spectroscopy. The transition from low spin to high spin around 400 K results in a crystallographic phase change, which causes a shattering of the crystals and which leads to a large hysteresis in the magnetic moment upon cooling from 460 to 250 K. Analysis of the Fe–N stretching band in the far IR was facilitated by ^{54}Fe/^{57}Fe substitution.[267]

An important class of binuclear iron Tp derivatives is exemplified by complex **102** which was synthesized as an analog of hemerythrin, having the proper type of one μ-oxo, and two μ-carboxylato bridges, with the Tp ligand mimicking three histidine residues. The initially prepared complex, with R = Me, was found to undergo easy exchange with CD$_3$COOD. The acetoxy bridge could also be exchanged with diphenyl phosphate, yielding the complex **103**.[268] Complex **102**, and its phosphinato analog **103**, were structurally characterized. It was shown that the diiron(III) core is expanded in both compounds relative to the dicarboxylate-bridged moieties. These complexes were also studied by NMR and Mössbauer spectroscopy.[269] Resonance Raman spectra and the excitation profile for **102** were determined and analyzed in detail.[270] Compound **102** was studied as a model for methane monooxygenase. It was found to catalyze the oxidation of adamantane and cyclohexane in methylene chloride with dioxygen, in the presence of acetic acid and zinc. The products from adamantane were the tertiary hydroxy > secondary hydroxy > keto derivatives; cyclohexane yielded mainly cyclohexenone, 2-hydroxycyclohexene, and cyclohexene



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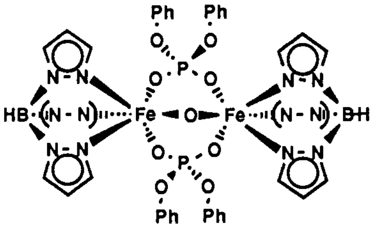

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epoxide. No reaction took place in the absence of either zinc or acetic acid, and other iron complexes gave only traces of products.[271]

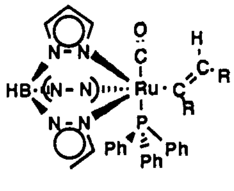
Complex **102** was studied and compared with other dinuclear Fe(III) complexes containing a similar core, and also with some enzymes, such as ribonucleotide reductase, methane monooxygenase, and others. The studies included EXAFS,[272-274] hydrogen and deuterium NMR, focusing on differences in chemical shifts for diverse different carboxyl residues (including also the μ-hydroxo analog of **102**),[275] electronic and Raman spectroscopy,[276] electronic and vibrational spectroscopy,[277] spin-exchange coupling,[278] comparison with the purple acid phosphatase from beef spleen,[279] comparison of its Mössbauer,[280] and structural, magnetic, and spectroscopic[281,282] parameters with those of related complexes. Complex **102**, along with related compounds, was discussed in a review of oxo- and hydroxo-bridged diiron complexes.[283]

The ligand Tp was also employed in blocking three coordination sites at the corners of $[Fe_4S_4]^{2+}$ clusters[284,285] and also in related $[VFe_3S_4]^{2+}$ clusters.[286]

Complexes Tp$_2$Ru, pzTp$_2$Ru, TpRu(PhCN)$_2$Cl, and pzTpRu(PhCN)$_2$Cl were prepared, and the latter two were studied as catalysts for olefin hydrogenation. They were active, with turnover numbers up to 200; methyl acrylate was hydrogenated to methyl propionate, while allylbenzene was partly hydrogenated to propylbenzene, and partly rearranged to the two isomers of propenylbenzene.[287] The novel Ru-NO complexes, TpRuNOCl$_2$, pzTpRuNOCl$_2$, Tp*RuNOCl$_2$ were prepared, and characterized by ^{1}H, ^{13}C, and ^{11}NMR, including ^{1}H NOE and ^{1}H-^{12}H and ^{13}C-^{1}H COSY, for assignment of individual protons and carbons.[288] Also prepared and characterized were the mixed sandwich complexes TpRuCp[289,290] and also Tp*RuCp, pzTpRuCp, and TpRuCp*. The structure of TpRuCp was determined by X-ray crystallography (Ru-C 2.153 Å and Ru-N 2.128 Å), and the above complexes were studied by cyclic voltammetry, where they exhibit quasireversible one-electron oxidation. Complexes η^2-Tp*RuCp(CO), η^2-pzTpRuCp(CO), and [pzTpRu$_2$Cp$_2$(CO)$_2$]PF$_6$ which contains bis-bidentate pzTp ligand. Tp*RuCp was oxidized and isolated as [Tp*RuCp]PF$_6$.[291]

The reaction of organoruthenium complexes, such as (organyl)Ru(PPh$_3$)$_2$(CO)Cl with TpK, yielded several types of products, depending on the organyl substituent. Prepared in this fashion were complexes **104–106**, and the structure of **106** was determined by X-ray crystallography.[292,293] The dimeric species [TpRu(CO)$_2$]$_2$ was synthesized, and its structure was determined by X-ray crystallography. It contains a Ru-Ru bond of 2.882(1) Å length, with each Ru being in a distorted octahedral geometry. Similarly prepared were the dimeric complexes [pzTpRu(CO)$_2$]$_2$, [TpOs(CO)$_2$]$_2$, and [pzTpOs(CO)$_2$]$_2$, as well as the monomeric species TpRu(CO)$_2$Cl, pzTpRu(CO)$_2$Cl, TpOs(CO)$_2$Br, and pzTpOs(CO)$_2$Br. The last two complexes in each category are the first examples of osmium homoscorpionates. Variable-temperature NMR spectra of pzTp complexes indicate interconversion of the coordinated and uncoordinated pz groups. This occurs easily with the Ru compounds, but sluggishly with the Os analogs.[294]

The crystallographically characterized TpRu(PPh$_3$)$_2$-Cl upon treatment with $[B_3H_8]^-$ provided the complex TpRu(PPh$_3$)(B$_3$H$_8$).[295]



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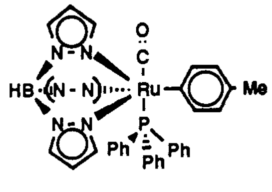

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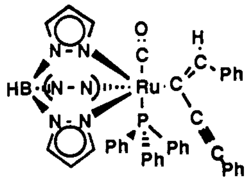

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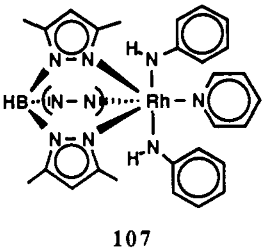
8. Group VIII: Co, Rh, Ir

The paramagnetic complex Tp$_2$Co induces shifts in the NMR spectra of molecules in its proximity. This effect of Tp$_2$Co and Tp*$_2$Co was studied for saturated hydrocarbons,[296] for a variety of nitrogen ligands in the second coordination sphere,[297] and for aromatic nitro compounds.[298]

The first complexes containing a homoscorpionate and a dicarbollide ligand on the same metal were prepared by the reaction of *closo*-3,3-(PPh$_3$)$_2$-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$ with TpK. The structures of the product *closo*-3-(Tp)-3,1,2-RhC$_2$B$_9$H$_{11}$ and of its isomer *closo*-2-(Tp)-2,1,7-RhC$_2$B$_9$H$_{11}$ were established by X-ray crystallography, confirming the mixed sandwich structure. NMR spectra show all three pz groups identical, implying facile rotation around the B–Rh axis. The reaction of TpK and Na$_2$[*nido*-7,8-C$_2$B$_9$H$_{11}$] with CoCl$_2$ yielded a salt consisting of $[Tp_2Co]^+$ cations and [*commo*-3,1,2-Co(3,1,2-C$_2$B$_9$H$_{11}$)]$^-$ anions.[299] Another unusual mixed sandwich complex containing boron-based ligands, TpRh(C$_4$H$_4$BPh), was prepared and characterized.[300]

A detailed study of ^{103}Rh NMR for a large number of Rh derivatives, including pzTpRh(COD) and pzTpRh(NBD) was carried out,[301] as was a study of chemical shift anisotropy relaxation in ^{103}Rh NMR. A linear relationship was found between the ^{103}Rh spin–lattice relaxation and the square of the magnetic field.[302]

The reaction of Tp*RhCl$_2$(Py) with LiNHPh produced Tp*RhCl(NHPh)(Py) or, when excess of LiNHPh was used, Tp*Rh(NHPh)$_2$(Py) (**107**), the structure of which was determined by X-ray crystallography. When Tp*RhCl$_2$(lutidine) was treated with LiNHPh, the complex Tp*Rh(NHAr)$_3$Li was obtained (Ar = Ph, *p*-tolyl). Since it was nonconductive, it was proposed that lithium is coordinated to the three nitrogen atoms in the inner coordination sphere. Use of LiNHBu^t in the above reactions led to reduction of Rh(III).[303]



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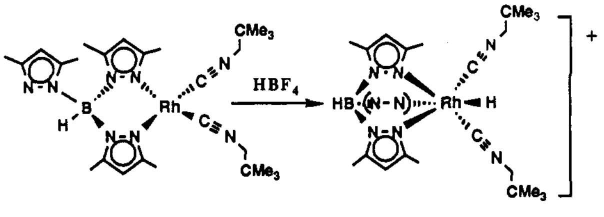
The structure of octahedral TpRh(I)(Me)(PPh$_3$) was established by X-ray crystallography.[304] The structures of Tp*Rh(CNR)$_2$ for R = neopentyl (108) and 2,6-xylyl were also determined. They contain bidentate Tp*, and the uncoordinated pz* group is positioned flatly above the square-planar Rh. Upon reaction with HBF$_4$ it is not the free pz* group that gets protonated, but rather Rh, which assumes octahedral coordination in the cation 109.[305] Complex 108 was prepared by the reaction of Tp*Na and neopentyl isocyanide with [RhCl(C$_2$H$_4$)$_2$]$_2$. Upon irradiation in benzene, one isonitrile is removed, and benzene adds oxidatively, forming the octahedral product Tp*Rh(CNR)(H)(Ph).[306] Phenyl azide adds to 108 and to related diisonitrile compounds, forming in regiospecific manner the carbodiimide complexes of structure Tp*Rh(CNR)(η^2-PhN=C=NR), where R = methyl, neopentyl, 2,6-xylyl. Reaction of 2,4-xylyl azide with Tp*Rh(CN-2-tolyl)$_2$ yields Tp*Rh(CN-2-tolyl)(η^2-2,4-xylyl-N=C=N-2-tolyl), the structure of which, 110, was determined by X-ray crystallography. It shows bidentate bonding of the carbodiimide ligand, with the azide-derived nitrogen bonded to Rh. In contrast to its Cp* analog, complex 108 upon irradiation (or thermally, though at a lower rate) loses one RNC group and oxidatively adds benzene, with a quantum yield of 1.0 ± 0.3. Photolysis of 108 in the solid state produces intramolecularly Tp*Rh(H)[2-(N=C=N-neopentyl)C$_6$H$_4$](CN-neopentyl), while addition of excess neopentyl isonitrile to 108 yields the azametallacyclobutane complex Tp*Rh(=N-neopentyl)N(Ph)C(=N-neopentyl)(CN-neopentyl) (111), for which an alternative structure is 112.[307] The mechanism of benzene loss from Tp*Rh(H)(Ph)(CN-neopentyl) in a thermolytic process has been studied, using fully deuterated THF and benzene as solvents. From the kinetics of this reaction, a mechanism has been proposed, which involves initialy reductive elimination of benzene, to give a η^2-benzene intermediate, in which the Rh atom can migrate around the benzene ring. The associative exchange of isocyanide for benzene occurs in the second step.[308]



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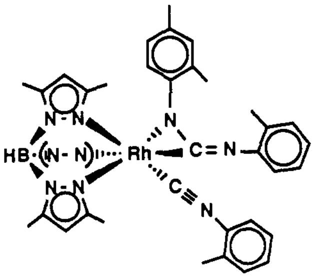

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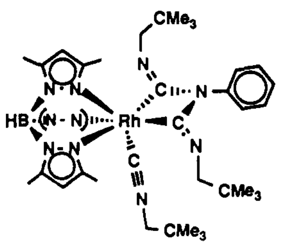

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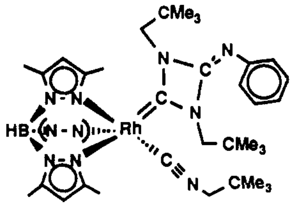

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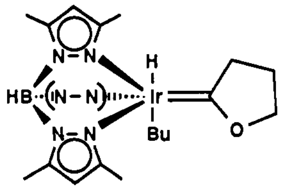
The first "nonclassical" polyhydrido complex stabilized by a nitrogen ligand, Tp*Rh(H$_2$)H$_2$, was synthesized by the reaction of [PPh$_4$][Tp*RhCl$_3$] with NaBH$_4$. The structure was assigned on the basis of a 2D (^{1}H,^{103}Rh) NMR study.[309]

Tp*–rhodium complexes showed interesting activity in C–H bond activation. Thus, irradiation of TpRh(CO)$_2$ in benzene or in an alkane, resulted in dissociation of one CO, and insertion of the appropriate H and R moieties, to yield the octahedral Tp*Rh(CO)(H)(R). Examples of R were phenyl, cyclohexyl, and methyl. The cyclohexyl derivative is the least stable and is readily converted upon reaction with CCl$_4$ to Tp*Rh(CO)(Cl)(R); it also equilibrates in the dark with methane.[310] In this and in other reactions of Tp*Rh carbonyl species, the denticity of the Tp* was monitored by IR. Complexes Tp*Rh(CO)(η^2-alkene), upon heating in benzene in the dark, lose the alkene and yield the oxidative addition product of benzene, Tp*Rh(CO)(H)(Ph), in high yield. The equilibrium constant for the reaction, when the alkene was cyclooctene, is 0.016 at 100 °C.[311] Ultraviolet irradiation of Tp*Rh(CO)(η^2-C$_2$H$_4$) in benzene yielded the two products: Tp*Rh(CO)(H)(Ph) and Tp*Rh(CO)(C$_2$H$_5$)(Ph), the latter one resulting from ethylene insertion. The structure of octahedral Tp*Rh(CO)(C$_2$H$_5$)(Ph) was confirmed by X-ray crystallography. This complex reacts with CO yielding the insertion product Tp*Rh(CO)[C(O)C$_2$H$_5$](Ph).[312]

The two analogous complexes, Tp*Rh(CO)$_2$ and Tp*Ir(CO)$_2$, behave quite differently upon protonation. The former is protonated on the nitrogen of the uncoordinated pz* group, yielding [[(Hpz*)HB(pz*)$_2$]Rh(CO)$_2$][BF$_4$]. The latter, by contrast, is protonated on the metal, forming the octahedral cation [Tp*Ir(CO)$_2$H]$^+$, containing Ir(III). [Tp*Ir(CO)$_2$H]$^+$ does not react with triethylamine, but is deprotonated to the starting material by (1,8-diazabicyclo[5.4.0.]undec-7-ene). Strong nucleophiles, such as NaOMe or BuLi, attack at the carbonyl carbon, forming Tp*Ir(CO)(H)(COOMe) and Tp*Ir(CO)(H)[C(O)Bu], respectively.[313]

The complex pzTpIr(COD) was synthesized and was converted to pzTpIr(CO)$_2$ by bubbling CO through a solution of the former. Both compounds were characterized by IR and NMR.[314] The complex TpIr(CO)$_2$ was characterized by IR, and its net electron donor strength was compared with that of other ligands. It failed to catalyze the reaction of triethylsilane with phenylacetylene.[315] The reaction of TpK with [Ir(olefin)Cl]$_2$ in THF yields in the case of ethylene TpIr(C$_2$H$_4$)$_2$, but with cyclooctene (COE), the product is the hydrido π-allyl complex, TpIr(H)(η^3-cyclooctenyl), TpIr(C$_2$H$_4$)$_2$ is converted by CO to TpIr(CO)$_2$, while on irradiation it forms Tp(η^2-CH$_2$=CH$_2$)(H)(η^1-CH=CH$_2$).[316] When the reaction of [Ir(COE)Cl]$_2$ with [Tp]$^-$ is done in methylene chloride, the product was the vinyl hydrido complex, $TpIr(H)(\sigma\text{-}C_8H_{13})(\eta^2\text{-COE})$, the structure of which was established by X-ray crystallography.[317] Hydrogenation under high pressure of Tp*Ir(COD) yielded $Tp^*IrH_2(\eta^2\text{-COE})$; at lower pressures a mixture of $Tp^*IrH_2(\eta^2\text{-COE})$ and $Tp^*IrH_2(\eta^2\text{-COD})$ was obtained. The complex Tp*Ir(COD) is protonated on pyrazole nitrogen, forming the cation $[(Hpz^*)HB(pz^*)_2Ir(COD)]^+$. Analogous complexes based on Tp^{Me_3} are also described. The very stable complex $Tp^*IrH_2(\eta^2\text{-COE})$ was structurally characterized by X-ray crystallography. Extended Hückel calculations were used to analyze the unusual alkene orientation in this complex.[318] Thermal rearrangement of $Tp^*Ir(C_2H_4)$ at 60 °C leads to the hydrido-π-allyl complex, $Tp^*Ir(H)(\eta^3\text{-}CH_2CHCHCHMe)$. The octahedrally coordinated vinyl hydride species, $Tp^*Ir(H)(CH{=}CH_2)(C_2H_4)$ is an intermediate in this reaction, as was proven by independent synthesis of $Tp^*Ir(H)(CH{=}CH_2)(C_2H_4)$ and its conversion to $Tp^*Ir(H)(\eta^3\text{-}CH_2CHCHMe)$.[319]

When $Tp^*Ir(C_2H_4)_2$ is heated in THF, two products are obtained: $Tp^*Ir(H)(\eta^3\text{-}CH_2CHCHMe)$ and the octahedral complex **113**, arising from double dehydrogenation of one of the α-methylene groups of tetrahydrofuran. Its structure was determined by $^1H\text{-}^{13}C$ NMR and by X-ray crystallography. Similar products were obtained from 2-methyltetrahydrofuran, dioxole, and dioxan, but not from tetrahydropyan.[320]



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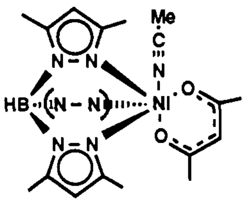
9. Group VIII: Ni, Pd, Pt

The complex TpNi-π-allyl was prepared from $[\pi\text{-allylNiCl}]_2$ and TpK, and its structure was determined by X-ray crystallography.[321] A variety of heteroleptic complexes, Tp*NiLL, was prepared by the treatment of Tp*Ni(AcAc), itself obtainable through the reaction of Tp*K with $Ni(AcAc)_2$, with the anions of the following active hydrogen compounds: MeCOOH, PhCOOH, $(PhO)_2POOH$, 2-mercaptopyridine, and thiosalicylic acid. The resulting green products were five-coordinate; they react with good donor solvents, yielding six-coordinate Tp*Ni(LL)S species, which slowly lose solvent on storage. Structures of the complexes **114**–**116** were established by X-ray crystallography, as was the structure of the five-coordinate Tp*Ni(PhCOO)[322] and of the five-coordinate Tp*Ni(OAc).[323]



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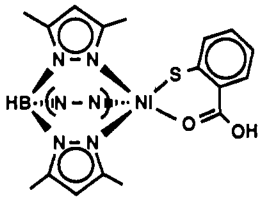

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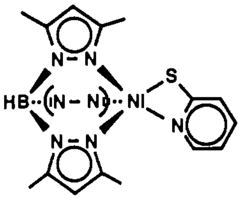
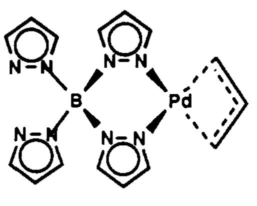


116

The complex Tp_2Pd has the metal in a square-planar configuration, with the two uncoordinated pz groups in the pseudoaxial positions above and below the coordination plane. They do not interact in any way with Pd.[324] The same holds true for $pzTp_2Pd$, which contains the metal in a square-planar environment, with bidentate ligand. NMR spectroscopy indicates the presence of a relatively low-energy process interconverting the two uncoordinated pz groups, but they do not exchange with the coordinated ones up to 25 °C. The two uncoordinated pz groups have been used to prepare complexes, such as $[pzTp_2Pd][ZnCl_2]_2$ and $[pzTp_2Pd][PdCl_2]_2$.[325] Additional examples of bidentate, and bis-bidentate pzTp coordination in Pd(II) complexes were obtained by the reaction of pzTpK with $[(\eta^3\text{-allyl})PdCl]_2$ which leads to $(pz)_2B(pz)_2Pd(\eta^3\text{-allyl})$ complexes **117**. These still retain the chelating ability of the $(pz)_2B$ portion of the molecule, and they form upon reaction with additional $[(\eta^3\text{-allyl})PdCl]_2$ the spiro-cations **118**, isolated as $[PF_6]^-$ salts. Similar cations were also prepared, based on poly(pyrazolyl)pyrazaboles.[326] NMR and electrochemical studies of $pzTpPd(PPh_3)(COFc)$ and $TpPd(PPh_3)(COFc)$ have been reported (Fc = ferrocenyl). The complexes contain four-coordinate, square-planar Pd. At 51 °C the environments of all pz groups are averaged, and only one set of pz signals is observed. These compounds undergo one-electron reversible oxidation, attributed to the Fe(II) ⇔ Fe(III) process.[327]



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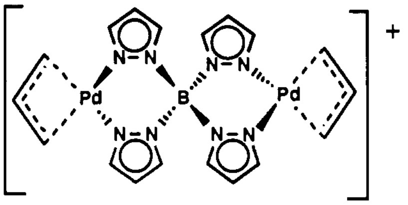
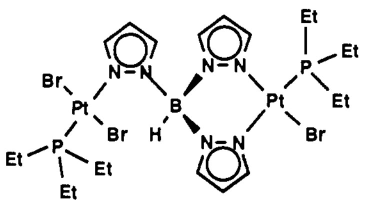


118

The only structurally characterized example of Pd(IV), $TpPdMe_3$, contains octahedrally coordinated Pd, and the molecule is of C_{3v} symmetry and of local C_{3v} symmetry in the case of $pzTpPdMe_3$.[328]

Tp^*PtMe_3 was obtained quantitatively from the reaction of $PtMe_3I$ with Tp*K. This complex reacts with bromine, yielding 4-brominated derivatives, the integrity of the Pt–Me bonds being maintained.[329] The reaction of pzTpK with $[Pt(PEt_3)_2(Br_2)]$ produced the five-coordinate complex $pzTpPt(PEt_3)Br$. By contrast, TpK formed, in the same reaction, a dinuclear complex, **119**, the structure of which was established by X-ray cyrstallography.[330]

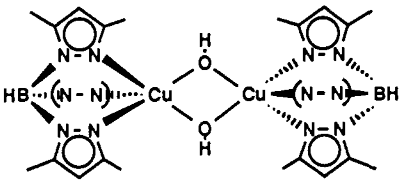


119

10. Group IB: Cu, Ag, Au

The structures of Tp_2Cu[331] and Tp^*_2Cu[332] were established by X-ray crystallography. Both complexes are octahedral with approximate D_{3d} symmetry. A correction of the space group used for the Tp^*_2Cu study, resulted in a more reasonable structure.[333]

Dinuclear copper complexes, based on Tp*, have been studied in detail as possible models for the enzyme oxyhaemocyanin (see related work with Tp^{iPr2}). The oxygen bridged species, $[Tp^*Cu]_2O$ was prepared by the reaction of Tp^*CuPPh_3 with PhIO. It reacts with PPh_3 regenerating the starting material, plus PPh_3O.[334] It also reacts with H_2O_2, yielding a dinuclear Cu(I) complex bridged by the peroxide dianion. The electronic spectrum of this complex resembles that of haemocyanin.[335] In terms of its chemistry, it does not oxidize PPh_3 or CO, yielding instead Tp^*CoPPH_3 and Tp*CuCO, respectively. Its oxidation of a variety of substrates, mostly phenols, was studied under aerobic and anaerobic conditions, and a mechanism was proposed for these oxygenation reactions, based on homolytic cleavage of the peroxide link, followed by free radical reactions.[336] Further elaboration of this class of complexes yielded the dimeric $[Tp^*Cu(OH)]_2$ (120) and the carbonato complex (121), arising from 120 upon reaction with CO_2. The structures of 120 and 121 and of Tp^*CuPPh_3 were established by X-ray crystallography.[337] This area of copper–dioxygen chemistry, and its relationship to biological systems, was discussed in review articles.[338,339]



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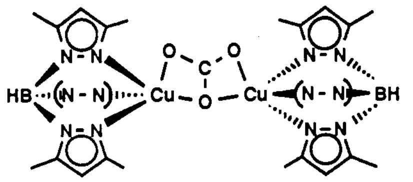


121

The gold(III) complex, $pzTpAuMe_2$, prepared from dimethylgold(III) nitrate and pzTpK, contains Au in square-planar coordination, with bidentate pzTp, as was established by X-ray crystallography. Variable-temperature NMR spectra of protonated species $[pzTpAuMe_2]H^+$ and $[TpAuMe_2]H^+$ indicate fluxional behavior, involving five-coordinate intermediates.[340]

11. Group IIB: Zn, Cd, Hg

Cadmium complexes Tp*CdR (R = Me, Et, nPr, iPr, all four Bu isomers, Ph) have been synthesized from KTp* and CdR_2 and fully characterized. The structure of Tp^*_2Cd was determined by X-ray crystallography.[341]

Complexes pzTpHgX (X = Cl, Br, I, NCS, OAc, CF_3COO, NO_3), as well as $pzTp_2Hg$, Tp*HgCl, and Tp_2Hg were prepared and spectroscopically characterized. Formation of analogous Tp complexes was prevented by the facile reduction of Hg(II); even with Tp* some reduction of Hg(II) to Hg^0 was observed, accompanied by the formation of the pyrazabole $(3{,}5Me_2pz)HB(\mu\text{-}3{,}5\text{-}Me_2pz)_2BH(3{,}5Me_2pz)$.[342]

The structure of pzTpHgMe was found to contain three-coordinate Hg with bidentate pzTp. The coordination is planar, but irregular: one Hg–N bond is short (2.07(4) Å), while the other Hg–N is much longer (2.65(4) Å). The uncoordinated pz groups are mutually orthogonal.[343] Complexes such as Tp*HgR (R = alkyl, aryl, ferrocenyl) were studied by ^1H, ^{13}C, and ^{199}Hg NMR; they are fluxional and are thought to contain two-coordinated Hg(II).[344]

12. Group IIIA: Al, Ga, In, Tl

The reaction of Tp*K with MCl_3 (M = Al, Ga) yielded salts $[Tp^*_2M][MCl_4]$. While the Al derivative did not provide good crystals for X-ray studies, the structure of $[Tp^*_2Ga][GaCl_4]$ was determined by X-ray crystallography. The cation contains Ga in an octahedral environment with overall D_{3d} symmetry. By contrast, the reaction of Tp*K with $InCl_3$ took a different course, and the resulting Tp^*InCl_2 complex was structurally characterized as the octahedral acetonitrile solvate.[345] Complexes Tp_2InCl, Tp_2InMe, $pzTp_2InCl$, and $pzTp_2InMe$ have been synthesized.[341]

While Tl(I) salts of homoscorpionate ligands were frequently used for the isolation and characterization of ligands and, because of their good solubility in hydrocarbon solvents, were often employed in metathetical reactions with organometallic halides, they were not studied per se. No Tl(III) polypyrazolylborates have been reported.

13. Group IVA: Si, Ge, Sn, Pb

The reaction of pzTpK with MCl_4 (M = Si, Ge, Sn) yielded complexes $pzTpMCl_3$. The $pzTpSiCl_3$ and $pzTpGeCl_3$ complexes were unstable, but were characterized by elemental analysis and by NMR.[346]

Homoscorpionate derivatives of Sn(II) include the structurally characterized Tp*SnCl and Tp^*_2Sn. In Tp^*_2Sn, one Tp* is three-coordinate, and the other Tp* is bidentate, with the lone pair occupying the sixth octahedral position. The coordinated and uncoordinated pz* groups exchange rapidly on the NMR time scale. The structure of Tp*SnCl is trigonal bipyramidal, with the lone pair occupying one apical site.[347] In the complex $pzTp_2Sn$ each ligand is bidentate, and the geometry around the tin atom is a highly distorted trigonal bipyramid. All pz groups are NMR equivalent at room temperature, while at −80 °C a 3:1 pattern emerges. Also prepared were Tp_2Sn, TpSnCl, and pzTpSnCl, and their ^{119}Sn NMR spectra were determined.[348] Additional Sn(II) complexes reported include $Tp^{Me}{}_2Sn$ and $Tp^{Me}SnCl$.[349]

Tin(IV) scorpionates were studied more extensively. $TpSnMe_nCl_{3-n}$ (n = 0–3) were prepared from TpK and the appropriate methyltin chlorides. They were studied by ^1H, ^{13}C, and ^{119}Sn NMR.[350] Similar complexes, based on Tp, pzTp, and Tp* ligands and containing in addition to Me and Cl, also Br, Et, Bu, and Ph substituents on the tin atom, were also synthesized and studied by ^{1}H ^{13}C, and ^{119}Sn NMR.[351-353] While the reaction of relatively concentrated solutions of pzTpK and Me_2SnCl_2 yields $pzTpSnMe_2Cl$, the same reaction in dilute solution produces the thermally sensitive $pzTp_2SnMe_2$, the NMR of which shows only one type of pz, implying a highly fluxional species. Complexes $pzTp_2SnEt_2$ and $pzTp_2SnBu_2$ were prepared analogously and had similar properties.[354] Several of the above compounds, as well as $TpSnPh_3$ and $TpSnBu_3$, were studied for antimutagenic activity.[355] The reaction of $TpSnCl_3$ with $[Co(CO)_4]^-$ produced, inter alia, the salt $[Tp_2Co]$[*trans*-$[[(CO)_4Co]Cl_2Sn]_2Co(CO)_3]^-$, the structure of which was determined by X-ray crystallography.[356]

The compound $TpSn(Cl_2)CH_2CH_2CO_2Me$ was prepared from TpK and $Cl_3SnCH_2CH_2CO_2Me$, and it was converted by treatment with KSCN to the octahedral, structurally characterized $TpSn(NCS)_2CH_2CH_2CO_2Me$ complex in which there is no coordination of the carbomethoxy group to Sn.[357] Also reported were triorganotin(IV) tetrakis(nitroindazolyl)borates of structure L^*SnR_3 (R = Me, Bu, Ph).[358]

Complexes Tp_2Pb, $pzTp_2Pb$, and Tp^*_2Pb were synthesized in good yield and, by using a 1:1 stoichiometry, complex TpPbCl was also prepared. The structures of $pzTp_2Pb$, Tp_2Pb, and Tp^*_2Pb were established by X-ray crystallography. In $pzTp_2Pb$ the ligand is bidentate, and the structure is trigonal bipyramidal, with the lone pair occupying one equatorial vertex. The NMR spectrum is dynamic, with all four pz groups equivalent at room temperature, but at −80 °C a 3:1 pattern emerges. By contrast, in both Tp_2Pb and Tp^*_2Pb, the ligands are tridentate. However, the structures are different: Tp_2Pb has a capped octahedron structure, with the lone pair in the capping position, while Tp^*_2Pb is octahedral, with an inactive lone pair.[359]

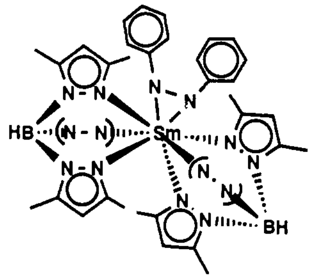
14. Group VA: P, As, Sb, Bi

The first example of a Tp^*PCl_2, was prepared from Tp*K and PCl_3, and upon reaction with $Na_2[Fe(CO)_4]$ afforded the compound $Tp^*PFe(CO)_4$, the structure of which was determined by X-ray crystallography. The complex contains bidentate Tp*, with the free pz* group totally uncoordinated.[360] The complex $pzTpAsMe_2$ has also been reported.[324] No Sb or Bi derivatives have been described.

15. The Lanthanides

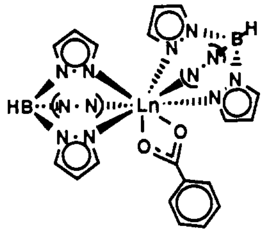
Complexes formed by Tp and pzTp with Tb(III) and Eu(III) were examined by IR, UV, and emission spectroscopy,[361] as were the Tp_3M species for M = Nd and Eu.[362] Complexes $Tp_2Y(H_2O)Cl$ and $Tp_2La(H_2O)Cl$ were prepared from Tp anion and the appropriate MCl_3 solutions. The eight-coordinate molecule has a "bent sandwich" configuration, as was established by X-ray crystallography for the yttrium complex, with cis relationship of the water and Cl ligands.[363] The reaction of YCl_3 with TpK in THF yielded $Tp_2YCl(THF)$, which existed in solution as a dimer–monomer equilibrium mixture. THF was readily displaced by Hpz, and the structure of $Tp_2YCl(Hpz)$ was determined by X-ray crystallography. It is similar to that of the $Tp_2Y(H_2O)Cl$ complex. Binuclear complexes $Tp_2Y(\mu\text{-}O_2CMe)_3YTp_2$ and $Tp_2Y(\mu\text{-}O_2CMe)_4YTp_2$ were obtained from TpK, TCl_3, and acetate ion, used in the proper stoichiometry. The structure of $Tp_2Y(\mu\text{-}O_2CMe)_4YTp_2$ was determined by X-ray crystallography. All these complexes exhibit dynamic NMR spectra.[364]

The air-sensitive Tp_2Sm and Tp_2Yb were prepared, and the structure of Tp_2Sm was determined by X-ray crystallography. The molecule is octahedral. It reacts readily with azobenzene, yielding the structurally characterized complex **122**, in which the azobenzene bond distances (1.334 Å) are midway between azobenzene (1.25 Å) and hydrazine (1.45 Å). Tp_2Sm is oxidized by Tl^+ to the cation $[Tp_2Sm]^+$.[36]



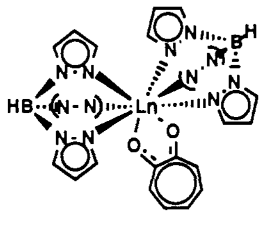
122

A large number of heteroleptic eight-coordinate lanthanide complexes of the type $Tp_2Ln(LL)$ has been synthesized, where LL were oxybidentate ligands which formed chelate rings of various sizes with the metal. A series of yttrium complexes of structure **123** was synthesized by the reaction of Tp and benzoate ligands (in 2:1) ratio with YCl_3, including those with para substituents (NO_2 and NMe_2) on the phenyl ring. When the para substituent was a *tert*-butyl group, the product was $TpY(O_2CC_6H_4\text{-}p\text{-}Bu^t)_2$.[365] Other monomeric complexes $Tp_2Ln(O_2CPh)$ (Ln = Y, Sm, Eu, Yb, Lu) and $Tp_2Ln(O_2CMe)$ (Ln = Y, Yb, Lu) were prepared. The structure of monomeric $Tp_2Y(OOCPh)$ was determined by X-ray crystallography.[366] Monomeric and fluxional complexes Tp_2LnCl, where Ln = Tb, Sm, Er, were synthesized. The analogous $Tp_2Ln(O_2CPh)$ complexes were dimeric, containing two μ-(O_2CPh) bridges, as was established for Ln = Sm by X-ray crystallography.[367] Also prepared were complexes $Tp_2Ln(O_2CPh)$, where Ln = Y, Sm, Eu, Yb, Lu, and $Tp_2Ln(O_2CMe)$, where Ln = Y, Eu, Gd, Yb, Lu. The species $Tp_2Ln(O_2CMe)$, where Ln = Ce and Sm, were unstable in solution and rearranged to Tp_3Ln. The structurally characterized complex $Tp_2Yb(O_2CPh)$ was monomeric.[368] The oxalato complexes $(Tp_2Ln)_2(C_2O_4)$, where Ln = Y, Sm, Dy, Yb, Lu, were prepared and characterized. These are dinuclear species, bridged by an oxalato unit, which forms two bidentate five-membered chelate rings.[369]



123

A series of tropolonate complexes Tp_2Ln(tropolonate), where Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Yb, Lu, was prepared. These compounds are unsolvated monomers of structure **124**, which was confirmed for $\mathrm{Tp_2Yb}$(tropolonate) by X-ray crystallography. Solubility trends, as a function of the lanthanide ionic radius, were noted.[368-370]



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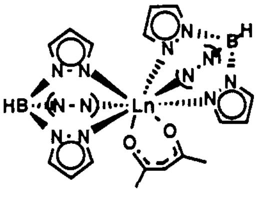


125

Another family of stable lanthanide complexes is exemplified by $\mathrm{Tp_2Ln}$(β-diketonate) (**125**). These complexes included $\mathrm{Tp_2Lu}$(dipivaloylmethanido), $\mathrm{Tp_2Yb}$(dipivaloylmethanido), $\mathrm{Tp_2Lu}$[3-(trifluoroacetyl)-D-camphorate], and $\mathrm{Tp_2Yb}$[3-(trifluoroacetyl)-D-camphorate]. They were characterized by ^1H and ^{13}C NMR and mass spectrometry, which showed the parent ion and the loss of β-diketone moiety. The structure of $\mathrm{Tp_2Yb}$(dipivaloylmethanido) was determined by X-ray crystallography.[371] An extended series of $\mathrm{Tp_2Ln}$(acac) complexes was prepared for Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu, and Y. While they all have structure **125**, X-ray crystallography shows that considerable distortion of the coordination geometry, found in the Ce(III) complex, is necessary for accommodating the smaller Yb(III) ion. Nevertheless, structure **125** can accommodate all lanthanide ionic sizes. NMR spectra indicate dynamic processes occurring intramolecularly down to −80 °C.[372,373] Similar series of $\mathrm{Tp_2Ln}$(β-diketonate) complexes were prepared using other β-diketonate anions: those from benzoylacetone (for Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Yb, Lu) and from dibenzoylmethane (for Y, La, Ce, Sm, Eu, Tb, Yb, Lu). The ligand exchange between these complexes was studied by NMR and was found to be a slow process, consistent with two opposing bimolecular reactions.[374]

16. The Actinides

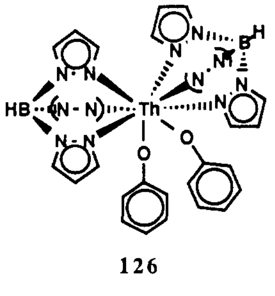
The reaction of $\mathrm{UCl_3}$ with Tp*K affords $\mathrm{Tp^*UCl_2}$.[375] The related complexes $\mathrm{Tp^*UCl_3}$(Hpz*), $\mathrm{Tp^*ThCl_3}$(Hpz*), and $\mathrm{Tp^*UCl_2}$(pz*) were prepared, starting with $\mathrm{UCl_4}$ or $\mathrm{ThCl_4}$ and Tp*K.[376] The U(IV) complex, $\mathrm{Tp^*UCl_3(THF)}$ was reduced with $\mathrm{NaC_{10}H_8}$ to $\mathrm{Tp^*UCl_2}$; similarly, the complex $\mathrm{Tp^*UCl_2[N(SiMe_3)_2]}$ was reduced cleanly to $\mathrm{Tp^*UCl_2[N(SiMe_3)_2]}$.[377] The structures of $\mathrm{Tp_2UCl_2}$ and $\mathrm{Tp_2ThCl_2}$ were determined by X-ray crystallography. The actinide center in both complexes is eight-coordinate and displays square antiprismatic geometry, distorted toward bicapped trigonal prismatic. The thorium complex shows more distortion than the uranium compound.[378]

The reaction of $\mathrm{Tp^*UCl_3(THF)}$, and of its Th analog, with the appropriate nucleophiles gave rise to complexes $\mathrm{Tp^*MCl_2Cp}$, $\mathrm{Tp^*MCl_2[N(SiMe_3)_2]}$, and $\mathrm{Tp^*M(NPh_2)_3}$, which were studied by IR and near-IR–visible and ^1H and ^{11}B NMR.[379] Complexes $\mathrm{Tp^*UCl_2Cp}$ and $\mathrm{Tp^*UCl_3}$ were structurally characterized; they both display six-coordination for uranium and octahedral geometry. The former complex has approximate C_s symmetry and the latter C_{3v}.[380] The structure of $\mathrm{Tp^*UCl_3(THF)}$ has also been determined by X-ray crystallography.[381] Sequential displacement of chloride ions in $\mathrm{Tp^*UCl_3(THF)}$ and $\mathrm{Tp^*ThCl_3(THF)}$ by appropriate nucleophiles (Cp and OR, where R = tBu, iPr, mesityl) has yielded complexes Tp*UCl(OR)(Cp) with asymmetric metal centers. The chiral characteristics of these complexes could be detected by their ^1H NMR spectra.[382]

Complexes containing both, Tp* and an alkoxide or aryloxide moiety on U(IV) and Th(IV) were prepared by the reaction of $\mathrm{Tp^*UCl_3(THF)}$ or $\mathrm{Tp^*ThCl_3(THF)}$ with the appropriate alkoxide or aryloxide ions. Complexes $\mathrm{Tp^*M(OR)_xCl_{3-x}}$ included those x = 1, 2, or 3, and R = iPr, tBu, mesityl. They were characterized by IR and near-IR-visible and ^1H NMR. Restricted rotation of the OR groups was indicated by variable-temperature NMR studies.[383] Similar complexes were also prepared using the Tp ligand instead of Tp*. The Tp ligands were fluxional, and the rotation of OR groups was restricted. From the temperature dependence of the NMR spectra, the rotational barriers were calculated.[384] The structure of $\mathrm{Tp^*UCl(OPh)_2(THF)}$ was determined by X-ray crystallography. The metal is seven-coordinate and displays capped octahedral geometry.[385] Structures of the Tp-based complexes, $\mathrm{Tp_2UCl(OPh)}$ and $\mathrm{Tp_2UCl(OBu^t)}$, were crystallographically characterized. Both complexes are eight-coordinate.[386]

The dialkoxo complex, $\mathrm{Tp_2U(OBu^t)}$, was prepared from $\mathrm{Tp_2UCl_2}$ and $\mathrm{NaOBu^t}$, and it was characterized by ^1H NMR. It contains fluxional Tp ligands.[387] Also reported, and structurally characterized was $\mathrm{Tp_2U(SPr^i)_2}$, in which the geometry around uranium approximates square antiprismatic, distorting toward dodecahedral. ^1H NMR shows fluxionality, with an activation energy of 46 ± 3 kJ mol^{-1}.[388] The above area was briefly reviewed, including the general reaction scheme for the products arising from the useful starting materials $\mathrm{TpUCl_3(THF)}$ and $\mathrm{Tp^*ThCl_3(THF)}$. The review also included the X-ray structure of the oxygen-bridged binuclear complex $\mathrm{[Tp^*Th(Cp)(Cl)]_2O}$.[389]

A more extensive series of $\mathrm{Tp_2Th(IV)}$ derivatives, including alkoxide, thiolato, aryloxide and alkyl substituents, was prepared, including species such as $\mathrm{Tp_2Th(SBu^t)_2}$ and $\mathrm{Tp_2Th(CH_2SiMe_3)_2}$. The structure of $\mathrm{Tp_2Th(OPh)_2}$ (**126**) was determined by X-ray crystallography. The eight-coordinate polyhedron around the thorium atom is square antiprismatic, with distortion toward dodecahedral.[390]



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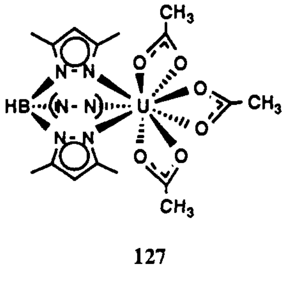

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Replacement of chloride ions in $\mathrm{Tp^*MCl_3(THF)}$ (M = U, Th) by acetate or benzoate ions produced complexes $\mathrm{Tp^*M(O_2CR)_3}$, which contained nine-coordinate actinide ion, as was shown by the X-ray crystallographic structure determination of the complex $\mathrm{Tp^*U(OAc)_3}$ (**127**).[391] Complexes $\mathrm{Tp_2(O_2CR)_2}$, where R = Me, $\mathrm{NMe_2}$, were reported as containing eight-coordinate U(IV).[392]

Compounds of the general type $Tp^*UCl_3(THF)$, $Tp^*ThCl_3(THF)$, Tp_2UCl_2, and $[Tp^*UCl_2]_x$ ($x = 1, 2$) were studied by laser desorption Fourier transform mass spectrometry.[393] The reaction–solution calorimetry measurements of the enthalpies of alcoholysis of a series of complexes Tp^*UCl_2L (L = OBu^t, $OCHBu^t{}_2$, $N(SiMe_3)_2$, $CH(SiMe_3)_2$ and C_5H_5) provided the actual values for these processes. Together with extended HMO calculations, they provided some explanation for the discrepancy between the uranium-ligand bond dissociation enthalpies obtained from iodinolysis and from alcoholysis reactions.[394]

The structure of $Tp^*UI_2(THF)_2$, prepared from Tp^*K and UI_3 in 1:1 ratio, was determined by X-ray crystallography and found to contain tridentate Tp* and the metal in a distorted capped octahedral geometry. This complex reacts readily with $[H_2B(pz)_2]^-$, forming the air-sensitive $Tp^*U[H_2B(pz)_2]_2$, characterized by NMR. When Tp^*K and UI_3 are reacted in 2:1 ratio, the product is $Tp^*{}_2UI$. In the crystal it contains one tridentate, and one bidentate Tp*, but the NMR spectrum is indicative of fluxionality. Its reaction with Tl^+ affords the cation $[Tp^*{}_2U(THF)]^+$, isolated as the BPh_4 salt.[36]

B. Heteroscorpionates

1. General

This group of complexes includes primarily those derived from previously reported ligands such as $[H_2B(pz)_2]^-$, $[Et_2B(pz)_2]^-$, $[Ph_2B(pz)_2]^-$, and $[H_2B(3,5\text{-}Me_2pz)_2]^-$. Heteroscorpionate ligands, $[HB(3Rpz)_2(5Rpz)]^-$ arising from intramolecular rearrangement of $[HB(3Rpz)_3]^-$ species are discussed along with the precursor ligands.

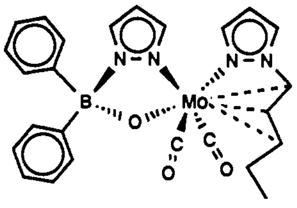
The ligand $[H_2B(pz)_2]^-$ was used in a study of M(II) extraction from aqueous media. The extraction constants of first-row transition metals increase in the order Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II), Be(II) is slightly extracted, but Mg(II), Ca(II), Sr(II), and Ba(II) are not extracted, regardless of the presence of synergists such as trioctylphosphine oxide or tetrabutylammonium chloride.[395] A series of anionic Fe(II), Co(II), and Ni(II) complexes, $Et_4N[M[H_2B(pz)_2]_3]$, containing three $[H_2B(pz)_2]^-$ ligands per metal was prepared in ethanol using the Et_4N^+ salt of the ligand; use of the K^+ salt led to simple $L^*{}_2M$ chelates. The $[L^*{}_3Fe]^-$ species is high spin.[396] The structure of the free acid, $H[H_2B(pz)_2]$, was established by X-ray crystallography.[397]

2. Individual Complexes

The complex $[H_2B(pz)_2]ZrCl_2(Cp)$ contains a three-center two-electron B–H–Zr bond, as was confirmed by NMR and by an X-ray crystallographic structure determination (H–Zr distance 2.27 Å). The agostic bond is broken upon coordination of Bu^tNC, which produces the complex $[H_2B(pz)_2]ZrCl_2(Cp)(Bu^tNC)$.[94]

Novel high-spin anionic five-coordinate Cr(II) and Mn(II) complexes of the type $[[H_2B(pz)_2]_2MCl]^-$ have been prepared, and the structure of $AsPh_4[[H_2B(pz)_2]_2MnCl]$ has been established by X-ray crystallography. The anion has a square-pyramidal structure, with the Cl atom at the apex and with Mn displaced by 0.52 Å above the pyramid base.[398] Oxidation of $[[H_2B(pz)_2]_2Cr(NCS)]^-$ yields $[[H_2B(pz)_2]Cr(NCS)]_2(\mu\text{-}OEt)_3$, structurally characterized by X-ray crystallography.[399] The reaction of $[H_2B(pz)_2]Mo(\equiv CAr)CO)(PX_3)_2$ with $Bu^tC\equiv P$ yielded the complex $[H_2B(pz)_2]Mo(\equiv CBu^t)(CO)(PX_3)_2$.[400] The structure of $Et_2B(pz)_2Mo(CO)_2(\eta^3\text{-allyl})$, which contains an agostic C–H···Mo bond was determined by X-ray crystallography, and a 2.11–2.24-Å value was obtained for the agostic H···Mo distance.[401]

The alkylidyne tungsten compounds $[H_2B(pz)_2]W(\equiv CR)(CO)_3$, where R = p-tolyl or Me, were studied by ^1H and ^{13}C NMR. The ethylidyne complex was of low stability, but $[H_2B(pz)_2]W(\equiv CAr)(CO)_3$ was stable and was readily converted to polynuclear derivatives. Thus, with $Co_2(CO)_8$ the trinuclear $[H_2B(pz)_2]W(\equiv CAr)Co_2(CO)_9$ was obtained, containing a $\mu_3\text{-}CCo_2W$ core, and similar to the analogous Tp-based structure. Reaction with $RhL_2(\eta^5\text{-}C_9H_7)$ produced the trimetallic $[H_2B(pz)_2]W(\equiv CAr)(CO)_3(\mu\text{-}CO)Rh_2(\eta^5\text{-}C_9H_7)$, and with $Fe_2(CO)_9$, the dimetallic $[H_2B(pz)W(\mu\text{-}CAr)(CO)_6$ was obtained. Substitution reactions of these complexes with phosphines and alkynes were studied.[402] The 16-electron complex $Ph_2B(pz)_2Mo(CO)_2(\eta^3\text{-pentadienyl})$ was structurally characterized by X-ray crystallography. Variable-temperature NMR indicated stereochemical nonrigidity, involving rotation around the B–Mo axis. Addition of phosphines or phosphites yielded 18-electron derivatives, while reaction with water hydrolyzed off one pz group, changing the $Ph_2B(pz)_2$ ligand to $Ph_2B(pz)(OH)$, and producing the complex 128, the structure of which was established by X-ray crystallography.[403]



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A (^{99m}Tc) technetium dihydrobis(pyrazol-1-yl)borate of undetermined composition was prepared, and its biodistribution in mice was studied by radiochemical analysis, with respect to myocardial perfusion imaging.[404]

The tetranuclear iron–oxo complex containing a $[Fe_4O_2]^{8+}$ core was synthesized from $[H_2B(pz)_2]K$, $(Et_4N)_2[Fe_2OCl_6]$, and RCOONa (R = Me or Ph). The structure of the product, $[H_2B(pz)_2]_2Fe_4O_2(PhCOO)_7$, was determined by X-ray crystallography. It was also studied by NMR and by solution-state magnetic susceptibility. The optical spectrum of this complex is similar to, but distinct from the analogous $[Tp_2Fe_2O(RCOO)_2]$.[405]

Different reaction courses took place in the reaction of $[H_2B(3,5\text{-}R_2pz)_2]K$ with $[(\eta^4\text{-}C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ and $[(\eta^4\text{-}C_8H_{12})RuCl(Me)(NCMe)]_2$, depending on the nature of R. With R = Me, complexes $[H_2B(3,5\text{-}Me_2pz)_2]Ru(\eta^4\text{-}C_8H_{12})X$ (X = H, Me) were obtained, which contained an agostic B–H···Ru bond, as was established by X-ray crystallography for the complex with X = H. By contrast, when R was Et or Ph, ligand fragmentation took place, and boron-free complexes were obtained, containing an amidine ligand, resulting from the addition of pyrazole to the acetonitrile solvent.[406] Cleavage of the $[H_2B(3,5\text{-}R_2pz)_2]$ ligand also occurred upon its reaction with *cis*-$RuCl_2(DMSO)_4$ in acetonitrile, and the structurally characterized product was $[Ru(pz)_2(Hpz)_3(DMSO)]$.[407] The complex *cis*-$[H_2B(pz)_2]_2Ru(PPh_3)_2$ was prepared from $RuCl_2(PPh_3)_2$ and was characterized by IR and by $^{31}P\text{-}^{1}H$ NMR.[408]

Complexes $[H_2B(pz)_2]Ir(COD)$ and $[H_2B(pz)_2]Ir(CO)_2$ have been prepared and characterized.[314]

The charge density and bonding in $[H_2B(pz)_2]_2Ni$ was determined by X–X_{HO}, multipolar analysis, and ab initio calculations. The experimental distribution of valence electron density was obtained from two sets of accurate diffraction data at 183 and 150 K and analyzed with the atomic multiple technique. Theoretical calculations were in reasonable agreement with these experimental results.[409] The mixed air-stable Ni(II) complex, derived from $Ph_2B(pz)_2$ and a carbollide ligand, $[\mathit{closo}\text{-}3\text{-}(Ph_2B(pz)_2)\text{-}3,1,2\text{-}NiC_2B_9H_{11}]Et_4N$, was synthesized and characterized by a combination of spectroscopic techniques and X-ray crystallography. The phenyl groups are almost orthogonal to each other, and they interchange via inversion of the $B(pz)_2Ni$ ring.[299] Electrochemical properties of the complex $H_2B(pz)_2Pd(COFc)(PPh_3)$, where Fc = ferrocenyl, were studied and compared with those of the Tp and pzTp analogs.[327] The complex $H_2B(pz)_2Pt(PEt_3)X$ (X = Cl, Br) was prepared, but could not be separated from an unknown impurity.[330]

The dinuclear anionic complex $[[H_2B(pz)_2Cu]_2(\mu\text{-}O)(\mu\text{-}pz)_2]^-$ was synthesized from copper(II) halides and $H_2B(pz)_2K$ in ethanol, containing a small amount of acetone, which degrades some of the ligand, leading to the above product, structurally characterized as the PPh_4^+ salt. The two copper atoms are antiferromagnetically coupled, with a singlet–triplet separation of $\simeq 240\ cm^{-1}$. Single-crystal EPR spectra indicated presence of exchange contributions to the anisotropic spin–spin interaction.[410]

The structure of complex $[H_2B(pz)_2]_3Y$ was determined by X-ray crystallography. The coordination around Y(III) is trigonal prismatic, and each of the three rectangular faces of the trigonal prism is capped by a three-center B–H···Y agostic bond. IR and NMR spectra indicate retention of these agostic bonds in solution. Low-temperature ^{13}C NMR shows two sets of pz groups in 1:1 ratio, suggesting a structure different from that in the crystal, and involving a twisting of the triangular face of the prism toward octahedral geometry. The molecule is fluxional in solution, all pz and BH_2 hydrogens becoming equivalent via a boat inversion mechanism. Similar fluxionality was also observed in $[H_2B(3,5Me_2pz)_2]_3Y$.[411] Luminescence spectra of the related $[H_2B(pz)_2]_3Tb$ complex were studied and found consistent with a trigonal-prismatic coordination, including weak agostic B–H···Tb bonds. In donor solvents the spectra change, indicating coordination of solvent molecules to Tb.[412] Similar $[H_2B(pz)_2]_3M$ complexes were also prepared for Sm and Er.[367] The isomorphous complexes $[H_2B(3,5Me_2pz)_2]_3M$ (M = Ce, Sm, Yb) were synthesized, and the structure of the Sm complex was established by X-ray crystallography. It is very similar to that of $[H_2B(pz)_2]_3Y$.[413]

Actinide heteroscorpionate complexes reported include $H_2B(pz)_2UCl_2(py)$ and $H_2B(3,5\text{-}Me_2pz)_2UCl_2$; the reactivity of $H_2B(pz)_2UCl_2(THF)$ with NaCp was also studied.[375] The structure of $[H_2B(3,5Me_2pz)_2]_3U$ was found to be identical with that of the analogous Ce, Sm, and Yb complexes. Also reported were $[H_2B(3,5Me_2pz)_2]_2UCl_2$ and $[H_2B(3,5Me_2pz)_2]_3U(OBu^t)_2$. During recrystallization of the former complex hydrolysis of the B–H bond in one of the ligands occurred, and a dinuclear complex was obtained. It contains two $[H_2B(3,5Me_2pz)_2][H(O)B(3,5Me_2pz)_2]U$ units, with the U atoms forming a $(UO)_2$ ring.[413]

Complexes $R_2B(pz)_2MEt_2$ (M = Al, R = Et; M = Ga, R = Et, Ph, pz) have been prepared by the reaction of $R_2B(pz)_2K$ with Et_2MCl.[346] The structure of the air- and moisture-stable $[H_2B(pz)_2]_2GaCl$, prepared from $H_2B(pz)_2K$ and $GaCl_3$ in 2:1 ratio, was established as trigonal bipyramid by X-ray crystallography.[414] The structure was refined to a greater degreee of accuracy.[415] The reaction of $GaCl_3$ with $H_2B(pz)_2K$ in 1:3 ratio produces $[H_2B(pz)_2]_3Ga$, while at a 1:1 ratio, the salt $[[H_2B(pz)_2]_2Ga][GaCl_4]$ is obtained. Similarly, by adjusting the component ratio, one can prepare $[H_2B(pz)_2]_2GaMe$ and $[H_2B(pz)_2]GaMe(Cl)$ from $MeGaCl_2$. The complex $H_2B(pz)_2GaMe_2$ was synthesized by several methods; one of its Me groups is solvolyzed with acetic acid, forming the octahedral $H_2B(pz)_2GaMe(O_2CMe)$, the structure of which was determined by X-ray crystallography.[416] A similar complex, $Me_2B(pz)_2GaMe_2$, was also prepared, and structurally characterized.[417]

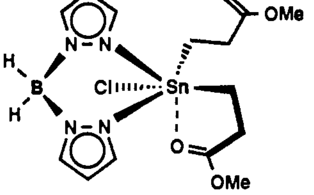
The octahedrally coordinated $[H_2B(pz)_2]_3In$ was prepared from $H_2B(pz)_2K$ and $InCl_3$ and structurally characterized by X-ray crystallography.[418] Depending on stoichiometry, complexes $H_2B(pz)_2InCl_2$ and $[H_2B(pz)_2]_2InCl$ can be prepared by the above reaction. Just as with Ga, the In compounds $H_2B(pz)_2InMe_2$, $H_2B(pz)_2InCl(Me)$, and $H_2B(pz)_2In(Me)(O_2CMe)$ were prepared, as was $[H_2B(pz)_2]_2In(O_2CMe)_2$. Structures of $H_2B(pz)_2InCl(Me)$ and $H_2B(pz)_2InMe_2$ were determined by X-ray crystallography. The former exists in the crystal as a chloride-bridged dimer with five-coordinate In, the latter contains indium in a tetrahedral environment.[419]

Reaction of $SiCl_4$ with $Ph_2B(pz)_2K$ at room temperature afforded octahedral $[Ph_2B(pz)_2]_2SiCl_2$, the structure of which was determined by X-ray crystallography. At higher temperatures, the pyrazabole $Ph_2B(pz)_2BPh_2$ was obtained. Similar cleavage reactions were observed in the reaction of $Ph_2B(pz)_2K$ with $GeCl_4$.[420]

Sn(II) complexes of heteroscorpionate ligands include $H_2B(pz)_2SnCl$, $Ph_2B(pz)_2SnCl$, $H_2B(3,5\text{-}Me_2pz)_2SnCl$ which contain four-coordinate tin (the lone pair occupying the fourth coordination site), $[H_2B(pz)_2]_2Sn$, $[Ph_2B(pz)_2]_2Sn$, and $[H_2B(3,5\text{-}Me_2pz)_2]_2Sn$.[350,351] Structures of $H_2B(pz)_2SnCl$ and $[H_2B(pz)_2]_2Sn$ were determined by X-ray crystallography. The former has a basic trigonal-pyramidal structure, with weak Sn–Cl bridging interactions, forming dimeric units in the crystal. The latter complex has a trigonal-bipyramidal structure, with each ligand spanning one axial and one equatorial site.[350]

Sn(IV) heteroscorpionates include the thermally fairly unstable and moisture-sensitive $[H_2B(pz)_2]_2SnMe_2$, $[H_2B(pz)_2]_2SnEt_2$, $[Et_2B(pz)_2]_2SnMe_2$, $[Et_2B(pz)_2]_2SnEt_2$, $[Et_2B(pz)_2]_2SnBu_2$, and $[Ph_2B(pz)_2]_2SnMe_2$. They are hydrolyzed to dimeric, (boryloxy)diorganyltin(IV) pyrazolides, $[R_2B(\mu\text{-}O)(\mu\text{-}pz)SnR'_2]_2$, and the structure of one of these complexes (R = Et, R′ = Me) was determined by X-ray crystallography.[354]

A more stable derivative was obtained from $H_2B(pz)_2K$ and $(MeO_2CCH_2CH_2)_2SnCl_2$, and its structure, 129, was established by X-ray crystallography. Tin is in a distorted octahedral arrangement, with one coordinated ester carbonyl group. The complex reacts with moist Na_2S, liberating the free acid, $H[H_2B(pz)_2]$.[397]



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The complex $[H_2B(pz)_2]_2Pb$ shows two dynamic processes in solution, as observed by ^{1}NMR spectroscopy: a low-barrier equilibration of the axial and equatorial pz rings in the pseudo-trigonal-bipyramidal structure and an inversion of the $B(pz)_2Pb$ rings, with a 9.4 kcal/mol barrier at −58 °C.[359]

IV. Concluding Remarks

Since the appearance of "second-generation" scorpionates, this area has been receiving increased attention, as researchers became more familiarized with this user friendly ligand system and started to appreciate the numerous ways of custom-tailoring and fine-tuning the environment of the coordinated metal in homoscorpionate complexes.

Some of the interesting new results reported within the last six years include reports on the synthesis and chemistry of monomeric MgR, ZnR, and BeX derivatives, of model complexes duplicating significant features of various copper- and zinc-based enzymes, and the extensive development of both low-valent and high-valent Mo and W chemistry. Several gaps in the periodic table have been filled, as scorpionates of Hf, Os, Be, Si, P, and As were reported for the first time; only a few main group scorpionate derivatives still remain unknown. The complex $[Tp^*W(NO)(Cl)NH(CH_2)_3P(Ph)_2]_2CdI_2 = C_{60}H_{78}B_2CdCl_2I_2N_{16}O_2P_2W_2$, containing 10 elements, has been cited as a world recordholder among known characterized compounds with most elements.[421]

Future developments in the homoscorpionate area will undoubtedly be built on the strengths of this system, i.e. on the ability to exercise a great degree of control on the environment of the chelated metal through appropriate substitution in the 3-, 4-, and 5-positions of the pyrazole ring. The most important mode of controlling the coordination is via regioselective introduction of 3R substituents, which have the most direct impact on accessibility of the coordinated metal to other reactants. At the same time, 4R substituents, while remote from the metal, can be used for increasing or decreasing the overall electron density of the ligand, via their electron-donating or -withdrawing properties. The 5R substituents tend to stabilize the ligand through steric protection of the B–H bond, and they can also tighten the ligand "bite" at the metal, through nonbonding repulsions at the boron end. Stabilization of the ligand can also be achieved through introduction at the boron atom of alkyl or aryl groups.

It is this multiplicity of options for precise tailoring of access space to a metal held by a homoscorpionate ligand, along with finetuning of the electron density through appropriate 4-substitution, that will probably see development in the years to come. This development is also likely to involve placement of additional coordinating substituents, including optically active ones, on the 3R group, for possible use in asymmetric synthesis, or in catalysis. Some of these developments are predicated upon the synthesis of novel, appropriately substituted pyrazoles.

Heteroscorpionates comprise an even larger area awaiting exploration, particularly ligands of the type $[RB(pz^*)_2(Z)]^-$, where Z can be OR, SR, NHR (R being either aliphatic or aromatic), leading to a tight complex with a deep boat structure, or CH_2OR, CH_2SR, and CH_2NHR, producing a shallower boat and looser structure. Of course, there are numerous other variations possible on the "sting" theme, and it will take some time before the full potential of the scorpionate ligand system is realized.

Note Added in Proof

The area of scorpionate chemistry remained quite active in the time interval between the submission of the manuscript and the proofing stage; 39 new articles were published (or are in the process of being published) prior to March 1993. They are briefly covered below.

a. Complexes of Ligands Other than Tp and Tp*. The salt $Tp^{tBu,Me}Tl$ has exact C_{3v} symmetry in the crystal, in contrast to $Tp^{tBu}Tl$, which has only local C_{3v} symmetry.[28] Tetrahedral complexes L^*ZnX ($L^* = Tp^{Ph}$, Tp^{Tol}, Tp^{An} and Tp^{Ph2}; X = Cl, Br, I, NO_3, Me, Et, Bu^t, Ph) have been prepared. The Zn-R derivatives were converted to Zn–OOCR, Zn–OSCR, Zn–SR, and Zn–SeR by treatment with the appropriate active hydrogen compounds. Crystal structures of $Tp^{Ph}Zn(NO_3)$, which contains an asymmetrically bidentate NO_3 ligand, $Tp^{Ph}ZnCl$, $Tp^{Ph}ZnSCOMe$, and $Tp^{Ph}ZnSEt$ were determined.[422] An improved synthesis of tetrakis(indazolyl)borate was published, along with some NMR studies.[424] The complex $Tp^{tBu,Me}ZnOH$ takes up CO_2 reversibly; it reacts with dialkyl pyrocarbonates, forming $Tp^{tBu,Me}ZnOCOOR$, and undergoes several other reactions functionally analogous to those of the enzyme carbonic anhydrase. The structure of complex $Tp^{tBu,Me}ZnOCOOMe$ was determined by X-ray crystallography.[423] The reaction of $Tp^{tBu}K$ or $Tp^{An}K$ with $Zn(ClO_4)_2{\cdot}6H_2O$ resulted in ligand hydrolysis and isolation of complexes $(H\text{-}3Bu^tpz^*)_3Zn(\mu\text{-}OH)Zn(H\text{-}3Bu^tpz^*)_3$.[425]

The tetrahedral thiolato complex $Tp^{iPr2}CuSC_6F_5$ was prepared and structurally characterized. This compound, and the analogous $Tp^{iPr2}CuSCPh_3$, showed spectroscopic similarity to the blue copper proteins azurin and plastocyanin.[426] These, and related copper complexes were discussed in a review of synthetic approaches to the structure and function of copper proteins.[427] Spectroscopic studies were carried out on two side-on μ-η^2:η^2 peroxide-bridged dimers $(Tp^{iPr2}Cu)_2(O_2)$ and $(Tp^{Ph2}Cu)_2(O_2)$, including assignment of peroxide-to-copper charge-transfer transitions. Isotopic shifts were used to assign four vibrational modes in the IR and Raman spectra for the two complexes. Their electronic structures were discussed in the context of various types of peroxide bridging and compared with those of natural oxyhemocyanin and oxytyrosinase.[428]

An asymmetric complex $\mathrm{Tp^{iPr2}Mn(\mu\text{-}OBz)_3Mn(H3,5Pr^i_2pz)_2}$ was synthesized and structurally characterized.[429]

Complexes $\mathrm{Tp^{An}Mo(NO)(CO)_2}$ and $\mathrm{Tp^{An}Mo(NO)Cl_2}$ were prepared and studied electrochemically. The structure of $\mathrm{Tp^{An}Mo(NO)(CO)_2}$ was determined by X-ray crystallography. It contains anisyl rings twisted by 52–62° with respect to the pyrazolyl plane.[430]

The first instance of an asymmetric tris(pyrazolyl)borate ligand, $\mathrm{[HB(3\text{-}mesitylpz)_2(5\text{-}mesitylpz)]^-}$, $\mathrm{Tp^{Ms*}}$, isomeric with $\mathrm{Tp^{Ms}}$, was synthesized and converted to derivatives $\mathrm{Tp^{Ms*}MX}$, $\mathrm{Tp^{Mx*}Pd(\eta^3\text{-}CH_2CMeCH_2)}$, $\mathrm{Tp^{Ms*}Rh(CO)_2}$, and others. The structures were confirmed by NMR, and that of $\mathrm{Tp^{Ms*}ZnI}$, by X-ray crystallography.[63]

Tin(IV) and organotin(IV) derivatives of $\mathrm{Tp^{Me}}$, of structure $\mathrm{Tp^{Me}SnCl_nR_{3-n}}$, have been synthesized and studied by ^{199m}Sn Mössbauer and NMR(^{1}H, ^{13}C, and ^{119}Sn) techniques. The structure of octahedral $\mathrm{Tp^{Me}SnCl_2Ph}$ was determined by X-ray crystallography.[431]

An improved synthesis of asymmetric bis(pyrazolyl)borates, $\mathrm{[H_2B(3,5\text{-}Me_2pz)(pz^*)]^-}$, has been reported. It is based on reacting the compound $\mathrm{H_2B(3,5\text{-}Me_2pzH)(I)}$ with various pyrazoles, Hpz*, yielding the unsymmetric cations $\mathrm{[H_2B(3,5\text{-}Me_2pzH)(Hpz^*)]^+}$, which can be deprotonated with NaH to $\mathrm{[H_2B(3,5\text{-}Me_2pz)(pz^*)]^-}$.[432]

b. Complexes of Tp and Tp* Ligands. The structure of $\mathrm{[pzTp]^-[H_3O]^+}$ was determined and found to be pseudoisomorphous with those of the pzTpNa and pzTpK salts.[433] The salts TpK and pzTpK were studied by means of negative-ion fast-atom bombardment mass spectrometry. Information on the ion structure was obtained from the collisionally activated dissociation spectra.[434] A detailed study of ion size discrimination in group II metals by poly(pyrazolyl)borate ligands showed strong dependence on the structural features of the resulting complexes, such as intraligand contacts, rather than on the basicity of the donor atoms Structures of the octahedral $\mathrm{Tp_2Mg}$, $\mathrm{Tp_2Ca}$, and $\mathrm{pzTp_2Mg}$, the tetrahedral $\mathrm{pzTp_2Be}$, and the cyclic trimer $\mathrm{[TpBe(OH)]_3}$, containing bidentate Tp, were determined.[435] Gas-phase photoelectron spectroscopy was used to study the complex $\mathrm{pzTp_2Fe}$ and establish the presence of a $^5T_2 \rightarrow {}^1A_1$ spin crossover under the experimental conditions.[436]

Good catalytic activity for carbene and nitrene transfer to form cyclopropanes, cyclopropenes, and aziridines was found in $\mathrm{Tp^*Cu(C_2H_4)}$. This complex operates under milder conditions than other catalysts in the carbene transfer from ethyl diazoacetate to alkenes or alkynes, and in nitrene transfer from PhI=NYs to alkenes.[437]

The 17-electron complex, $\mathrm{[Tp^*Mo(NO)(Cl_2)][HNEt_3]}$ was obtained upon reduction of $\mathrm{Tp^*Mo(NO)(Cl_2)}$ in the presence of triethylamine. Its reaction with pyridine produces $\mathrm{Tp^*Mo(NO)(Cl)(py)}$.[438] Electrochemical studies of the binuclear complex $\mathrm{[Tp^*Mo(NO)(Cl)]_2[1,2\text{-}(NH)_2C_6H_4]}$ revealed two one-electron reduction processes separated by 770 mV, and the structure was determined by X-ray crystallography.[439] In the compounds $\mathrm{Tp^*M(NO)(X_2)}$ (M = Mo, X = Cl, Br, I; M = W, X = Cl) one of the halogens can be replaced with an alkoxy group derived from various monosaccharides, and complexes $\mathrm{Tp^*M(NO)(X)(OR)}$, where ROH = 2,3:4,5-di-*O*-isopropylidene-*β*-D-fructopyranose, have been isolated as mixtures of diastereomers.[440] Reaction of $\mathrm{Tp^*Mo(NO)(Cl_2)}$ with sulfur afforded $\mathrm{[Tp^*Mo(NO)(Cl)]_2(\mu\text{-}S_2)}$, which contained the Mo–S–S–Mo core, as was determined by X-ray crystallography.[441] EPR, magnetic, and electrochemical studies of electron exchange and intermetallic interaction through polyene bridges were carried out on complexes of structure $\mathrm{[Tp^*Mo(NO)(Cl)]_2[4,4'\text{-}NC_5H_4(CH{=}CH)_n\text{-}H_4C_5N]}$.[442] Electrochemical studies were also conducted on related species, such as $\mathrm{Tp^*Mo(NO)(X)(NHC_6H_4CH{=}CHC_6H_4OR\text{-}4,4')}$ and $\mathrm{Tp^*Mo(NO)(NHC_6H_4CH{=}CHC_6H_4OR\text{-}4,4')_2}$, where R is a long-chain alkyl group,[443] as well as on $\mathrm{Tp^*Mo(NO)(X)}$(*O*-cholesteryl), where X is Cl, I, or octyloxy, and on $\mathrm{Tp^*Mo(NO)}$(*O*-cholesteryl)$_2$. They all undergo one-electron reduction processes.[444] A fully reversible, one-electron reduction was observed in $\mathrm{[Tp^*Mo(NO)(Cl)]_2(\mu\text{-}O)}$; the synthesis of two diasteromers of both $\mathrm{[Tp^*Mo(NO)(Cl)]_2(\mu\text{-}O)}$ and $\mathrm{[Tp^*Mo(NO)(Cl)](\mu\text{-}O)[Tp^*Mo(NO)(I)]}$ was reported.[445]

The structure of the seven-coordinate $\mathrm{TpMo(CO)_3CH_2CN}$ was determined crystallographically and found to contain a four-legged piano stool coordination for Mo.[446] Complexes $\mathrm{Tp^*Mo(CO)_2(\eta^3\text{-}crotyl)}$, $\mathrm{TpMo(CO)_2(\eta^3\text{-}cyclohexenyl)}$, $\mathrm{Tp^*Mo(CO)_2(\eta^3\text{-}cyclohexenyl)}$, $\mathrm{TpMo(CO)_2(\eta^3\text{-}cycloheptenyl)}$, and $\mathrm{Tp^*Mo(CO)_2(\eta^3\text{-}cyclooctenyl)}$ was prepared and converted to cationic complexes, such as $\mathrm{[Mo(CO)_2(\eta^4\text{-}cyclohexadiene)]^+[PF_6]^-}$ by treatment with $\mathrm{Ph_3CPF_6}$, and the crystal structure of $\mathrm{TpMo(CO)_2(\eta^3\text{-}cycloheptenyl)}$ was determined by X-ray crystallography.[447]

The complex $\mathrm{Tp^*Mo^{VI}O_2(SPh)}$ was found to display all the important centers and processes involved in the catalysis by molybdoenzymes containing $\mathrm{[Mo^{VI}O_2]^{2+}}$ active sites. In the course of demonstrating the diverse chemistry involved, the first dioxo-Mo(V) species, $\mathrm{[Tp^*Mo^VO_2(SPh)]^-}$, was isolated by one-electron reduction of $\mathrm{Tp^*Mo^{VI}O_2(SPh)}$.[448] A complex of relevance to the oxothiomolybdenum(VI) active site proposed for oxidized xanthine oxidase was prepared and structurally characterized. This distorted octahedral oxothiomolybdenum(VI) complex, $\mathrm{Tp^*Mo(OS)(\eta^2\text{-}S_2PPr^i_2)}$, shows some interaction between the MoS and P=S sulfur atoms.[449] The $\mathrm{[Tp^*Mo^VO]^{2+}}$ fragment was coupled to a tetraarylporphyrin Fe(III)Cl unit, yielding binuclear complexes with controlled Mo···Fe distances. EPR spectroscopy at 4 K indicated distance-dependent static dipolar coupling between Mo(V) and high-spin Fe(III). At 77 K the dipolar coupling was modulated by rapid relaxation of the Fe(III) center. The EPR spectra of iron-free complexes and of Mo(V)/Zn(II) analogs were unperturbed.[450a]

The use of $\mathrm{AlMe_3}$ permitted facile conversion of $\mathrm{Tp^*MO_2Cl}$ (M = Mo, W) to $\mathrm{Tp^*MO_2Me}$, and the structure of the Mo complex was determined by X-ray crystallography. Complexes $\mathrm{Tp^*WO_2(CH_2R)}$ were obtained by the reaction of $\mathrm{Tp^*WO_2Cl}$ with $\mathrm{RCH_2MgCl}$ (R = $\mathrm{SiMe_3}$, *t*-Bu, $\mathrm{CMe_2Ph}$, $\mathrm{C(Me){=}CH_2}$). The transylidation species, $\mathrm{Tp^*WO_2(CHPR_3)}$, were prepared from $\mathrm{Tp^*WO_2Cl}$ and $\mathrm{R_3P{=}CH_2}$.[450b]

Alkylation of $\mathrm{[Tp^*W(CO)_2(CNEt)]Na}$, which was prepared by sodium amalgam reduction of $\mathrm{Tp^*W(CO)_2(CNEt)(I)}$, with alkyl iodides (R = Me, Et) produced the spectroscopically characterized carbynes $\mathrm{Tp^*W(CO)_2({\equiv}CNEtR)}$.[451] The reaction of $\mathrm{Tp^*W({\equiv}CR)X_2}$ (R = t-Bu, X = Cl; R = Ph, X = Br) with neutral alumina or with aniline yielded the thermally stable complexes $Tp^*W(\equiv CR)(E)X$ where E = O or NPh and a member of this group, $Tp^*W(\equiv CBu^t)(O)Cl$ when combined with $AlCl_3$ catalyzed efficiently the acyclic diene methathesis (ADMET) of 1,9-decadiene, producing a mixture of 1,9,17-octadecatriene, 1,9,17,25-hexadodecatetraene, and ethylene.[452]

Photolysis of $Tp^*Rh(\equiv CN\text{-neopentyl})(\eta^2\text{-}PhN{=}C{=}N\text{-neopentyl})$ in various alkanes and arenes leads to elimination of the carbodiimide ligand, with formation of the oxidative adducts $Tp^*Rh(\equiv CN\text{-neopentyl})(R')H$. Aromatic hydrogens are activated in preference to benzylic ones, and aliphatic primary C–H bonds are preferred to secondary ones. Rates of reductive elimination of a variety of aliphatic and aromatic hydrocarbons were measured and used to establish relative Rh-R bond strengths for these ligands. The structure of the octahedral complex, $Tp^*Rh(\equiv CN\text{-neopentyl})(n\text{-pentyl})Cl$, was established by X-ray crystallography.[453]

The reactions of $TpIrH(CO)_2$ with H_2O, MeOH, or EtOH yielded TpIrH(COOH)(CO), TpIRH(COOMe)(CO), and TpIrH(COOEt)(CO), respectively. Similar reactions with the pzTp analogs proceeded less cleanly. Refluxing of TpIrH(COOMe)(CO) in acetonitrile produced $TpIrH_2(CO)$.[454] Similarly, upon reaction with primary amines, the corresponding carbamoyl complexes TpIrH(CONHR)(CO) were obtained and were characterized by IR and NMR spectroscopy. They react with HBF_4, forming the cations $[TpIRH(CO)_2)][BF_4]$.[455] The preparation of $TpIr(C_2H_4)(CO)$, $[TpIr(Et)(\eta^2\text{-}C_2H_4)][BF_4]$, and $[TpIr(Et)(CO)][BF_4]$, and their studies by NMR have been reported.[456]

Treatment of the pallada(IV)cyclopentane complex, $Pd[\eta^2\text{-}(CH_2)_4\text{-}](tmeda)$ with TpK, followed by addition of either methyl iodide or benzyl bromide, yielded $TpPd[\eta^2\text{-}(CH_2)_4\text{-}](R)$.[457] In a study of Pd(II) and Pt(II) complexes $pzTpM(PPh_3)X$ it was found that the activation energy for the $B(pz)_2M$ boat inversion decreases in the order X = I > Cl > Br > η^1-methallyl. Reaction of $pzTpM(\eta^3\text{-methallyl})$ complexes with Ag^+ or with $[M(\eta^3\text{-methallyl})]^+$ species yielded bimetallic complexes, which were studied by 1D and 2D NOE techniques. X-ray crystallography confirmed the spiro structure for $\{B[(pz)_2Pt(\eta^3\text{-methallyl})]_2\}PF_6$.[458] The organometallic chemistry of palladium and platinum with, inter alia, poly(pyrazolyl)borates has been reviewed.[459]

The complex $[Tp^*_2In]I$ was prepared and structurally characterized by X-ray crystallography, comparing the structure to that of $[MeGa(pz)_3]_2In[InL_4]$.[460]

V. References

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(4) In these, and in all subsequent drawings, –(N–N)– denotes the third pz* group, identical to the other two, and positioned edge-on below the paper plane.
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