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Recent developments in the chemistry of early transition metal porphyrin compounds

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Contents

Abstract

A review with 243 references on early metal porphyrins involving transition metals in groups 3–6 with special emphasis on out-of-plane metal porphyrins with cis-coordination is presented.

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The preparation and reactivity of metal porphyrins as well as the structural parameters of crystallographically characterized out-of-plane derivatives are discussed.

Keywords: Metal porphyrins; Transaction metals; Structural parameters

Abbreviations

$(OEP)^{2-}$	octaethylporphyrinato dianion
$(OMP)^{2-}$	octamethylporphyrinato dianion
$(TPP)^{2-}$	tetraphenylporphyrinato dianion
$(T\mathit{p}TP)^{2-}$	tetra-*p*-tolylporphyrinato dianion
$(T\mathit{m}TP)^{2-}$	tetra-*m*-tolylporphyrinato dianion
$(ETP)^{2-}$	etioporphyrinato dianion
$(DPEP)^{2-}$	deoxophylloerythroetioporphyrinato dianion
$(\mathit{meso}\text{-}DME)^{2-}$	*meso*-porphyrinato dianion-dimethylester
$[TH_{4py}P]^{2+}$	tetra-*p*-pyridiniumporphyrinato dication
py	pyridine
1-MeIm	1-methylimidazole
THF	tetrahydrofuran
Et_2O	diethylether
PBu_3	tributylphosphine
$PPhMe_2$	dimethylphenylphosphine
$(acac)^-$	acetylacetonato monoanion
$(OAc)^-$	acetate anion

1. Introduction

The field of porphyrin chemistry has expanded enormously since the last major reviews of porphyrin and metalloporphyrin compounds appeared [1,2]. Several review articles have been published in the meantime dealing with specific aspects of porphyrin chemistry and these subject areas need not be duplicated here [3–12]. Naturally, a great deal of attention has been focused on metalloporphyrins of Mn, Fe and Co owing to their significance in biological processes. In recent years, however, synthetic routes have been devised to prepare porphyrin derivatives of groups 3–6 which, in common with their non-porphyrin ligated counterparts, show significantly different structures and chemical reactivities compared with the late transition metal derivatives. Many of the differences are related, to some extent, to changes in the size, electronegativity, and/or stabilities of oxidation states of the metals concerned. For synthetic reasons, the emphasis in the early transition metals has so far been on the first row elements, since preparative routes to the heavier derivatives are less well developed and the resulting compounds are comparatively more labile.

The dimensions of the central core of porphyrin dianions are such that metal ions of radii 0.60–0.65 Å are accommodated in the plane of the N_4 ring [13–15]. For smaller ions, the entire ring can ruffle through an S_4-type deformation to reduce the hole size. If the metal is only slightly too large, the core can expand somewhat by doming to coordinate the ion. The vast majority of known porphyrin chemistry is based on derivatives involving late transition metals, where an in-plane geometry directs ligands to mutually trans positions in a distorted octahedral environment. For much larger metals, such as the heavier metals early in the transition series, however, the metal is displaced from the N_4 porphyrin plane. As a result, additional ligands on the metal are constrained to be 'sitting atop' or cis to one another, as invoked by Buchler and co-workers in 1971 [16–18]. Since then many examples of this type of coordination have been found for early transition metals in groups 3–6 (Scheme 1).

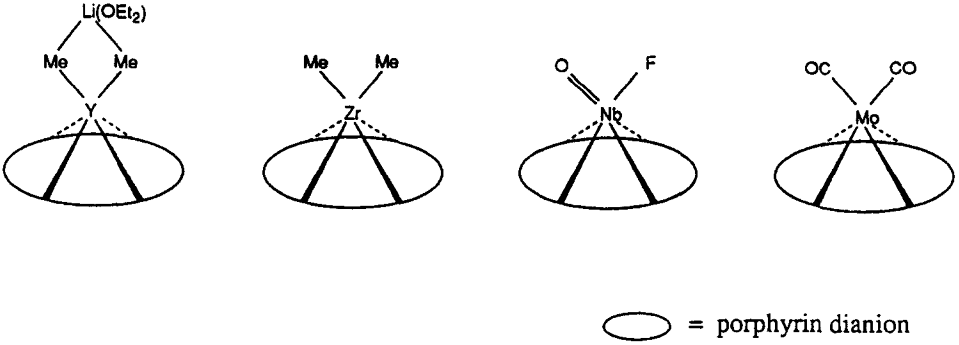
Cis coordination is a prerequisite for many established reaction pathways such as insertion of small molecules into metal alkyl bonds, reductive elimination and cyclization of small molecules. Owing to the lack of readily accessible cis coordination sites in late transition metal porphyrins, mechanisms involving free radicals dominate the reactivities of these compounds.

Here we review the more recent discoveries in early transition metal porphyrin chemistry, with specific emphasis on the more unusual out-of-plane metal porphyrins involving cis coordination.

2. Preparative procedures

2.1. From free-base porphyrins

Traditional preparative procedures to generate metalloporphyrins have been reviewed by Buchler [19]. In general, the free base porphyrin is reacted with a large excess of metal salt or metal carbonyl in high boiling solvents. The work-up usually requires chromatography and is therefore prohibitive for oxygen and moisture sensitive derivatives and not very convenient for large scale preparations (more than 5 g). Metal organyls provide an entry into these compounds employing rather mild reaction conditions. A recent example is depicted in Eq. (1) [20,21],



Scheme 1.

$$H_2(OEP)+Y[CH(SiMe_3)_2]_3 \rightarrow Y(OEP)[CH(SiMe_3)_2] \qquad (1)$$

2.2. From dilithium porphyrins

The isolation of alkali metal porphyrins opened an alternative route into functionalized metal porphyrins [22,23]. Lithium, sodium, and potassium derivatives with a wide range of alkyl and aryl-substituted porphyrins can be prepared and isolated on large scales (ca. 10–20 g). Yields of these highly crystalline compounds usually exceed 90%. The crystal structures of a variety of salts show that one Li prefers to bind at the center of the N_4 ring forming the anions $[Li(P)]^-$ (Fig. 1), whereas the larger Na and K derivatives form neutral out-of-plane $M_2(P)(solv)_4$ structures (solv ≡ THF, py).

Metathesis reactions with metal halides, such as that shown in Eq. (2), afford metal porphyrin compounds cleanly and in high yield. The Na and K salts may also be used; however, owing to the higher solubilities of the Li derivatives, these are generally preferred.

$$Li_2(OEP)(THF)_2+ZrCl_4(THT)_2 \rightarrow Zr(OEP)Cl_2 \qquad (2)$$

The advantages of the "dilithium-method" over many other routes are that large amounts (several grams) of metal porphyrins can be prepared in a reaction requiring

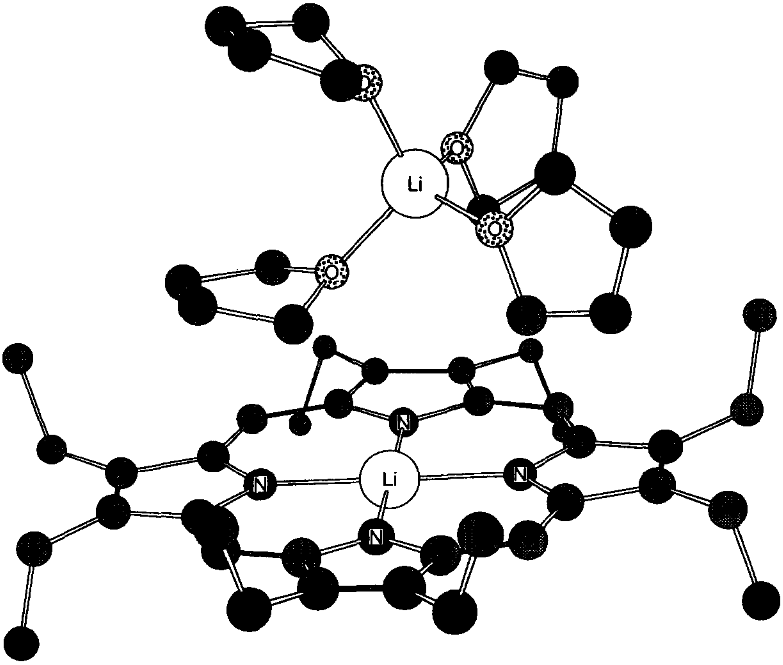


Fig. 1. Crystal structure of $Li_2(OEP)(THF)_4$ [23].

only low boiling solvents and stoichiometric amounts of porphyrin and metal salts. No chromatography is necessary as the work-up usually requires a simple recrystallization or soxhlet extraction. This method also allows metathesis of thermally sensitive functionalized metal halides such as $(Me_3SiCH_2)_2ZrCl_2(Et_2O)_2$ with the lithium porphyrin to afford dialkyl metal porphyrins (see below).

3. Group 3 metalloporphyrins

Sc(OEP)(acac) and Sc(OEP)(OAc) were first prepared by Buchler et al. in 1971 [16]. Their redox and reduction chemistry has been investigated [18,24]. The complex Sc(OEP)OSc(OEP) [25,26] is reported to be in equilibrium with the monomer Sc(OEP)OH as judged by UV–visible spectroscopy [25]; the physical properties of scandium mono-porphyrins and the μ-oxo complex have been thoroughly studied [27–29].

The first yttrium porphyrin complex Y(TPP)(acac) was described by Horrocks and co-workers [13,30] and a number of porphyrin sandwich compounds $Y(P)_2$ and the acac complexes Y(P)(acac) have been prepared [30]. Reaction of Y(P)(acac) with Schiff base compounds results in the formation of the pseudo sandwich compound Y(P)(L-4)(L-4 ≡ Schiff base) [31].

Organometallic OEP derivatives of Y and Lu were prepared from the corresponding metal organyls and the free base porphyrin (Eq. (3)) [20,21]. Protonolysis of $M(OEP)CH(SiMe_3)_2$ with $HO\text{-}2,6\text{-}C_6H_3^tBu$, HCC^tBu, or H_2O gave monomeric alkoxide and dimeric alkynyl and hydroxide species.

$$R_3M + H_2(OEP) \rightarrow M(OEP)R + RH \qquad (3)$$

$$R \equiv (Me_3Si)_2CH,\ o\text{-}2,6\text{-}C_6H_3^tBu;\ M \equiv Y,\ Lu$$

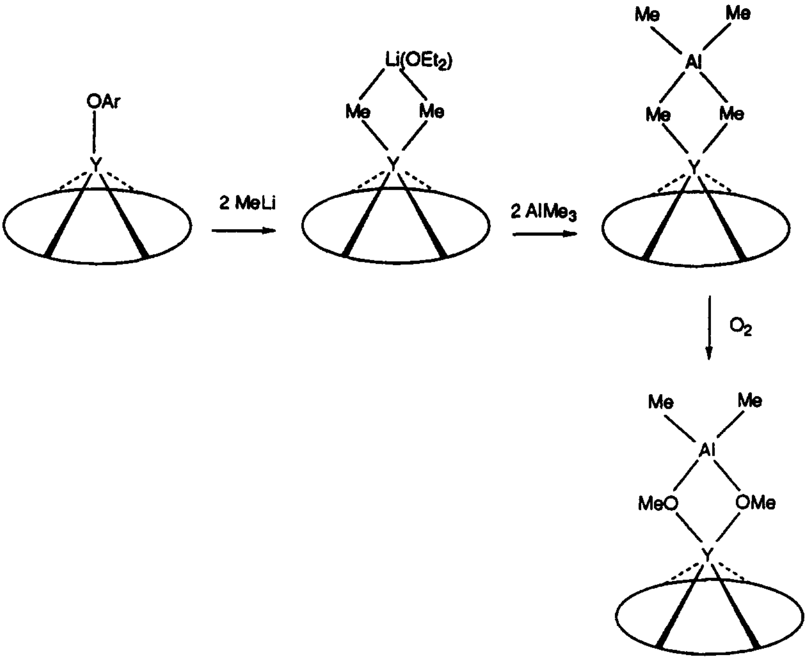
Reaction of the yttrium alkoxide with MeLi did not afford the expected pentavalent Y(OEP)Me but a species containing two methyl groups bridged by an Li cation, a result which highlights the tendency of the large Y(III) ion to form complexes with high coordination numbers. The Li could be removed by treatment with two equiv $AlMe_3$ affording $Y(OEP)(\mu\text{-}Me)_2AlMe_2$. This compound shows interesting reactivity towards dioxygen, reacting selectively with only one equivalent of dioxygen to form $Y(OEP)(\mu\text{-}OMe)_2AlMe_2$ (Scheme 2).

The proposed mechanism for this reaction involves attack of O_2 at the more oxophilic, less sterically hindered yttrium (as opposed to the four-coordinate aluminum) to form a bridging $Y(\eta^2\text{-}OOMe)Al$ species. Subsequent insertion into the remaining $Y(\mu\text{-}Me)Al$ entity yields the observed product.

More recently, multigram quantities of Sc(OEP)Cl were prepared straightforwardly by metathesis of $Li_2OEP(THF)_2$ and $ScCl_3(THF)_3$ in greater than 90% yield (Eq. (4)) [32,33];

$$Li_2OEP(THF)_2 + ScCl_3(THF)_3 \rightarrow Sc(OEP)Cl \qquad (4)$$

Sc(OEP)Cl was easily functionalized to give alkoxide, triflate, amide and organo-



Scheme 2.

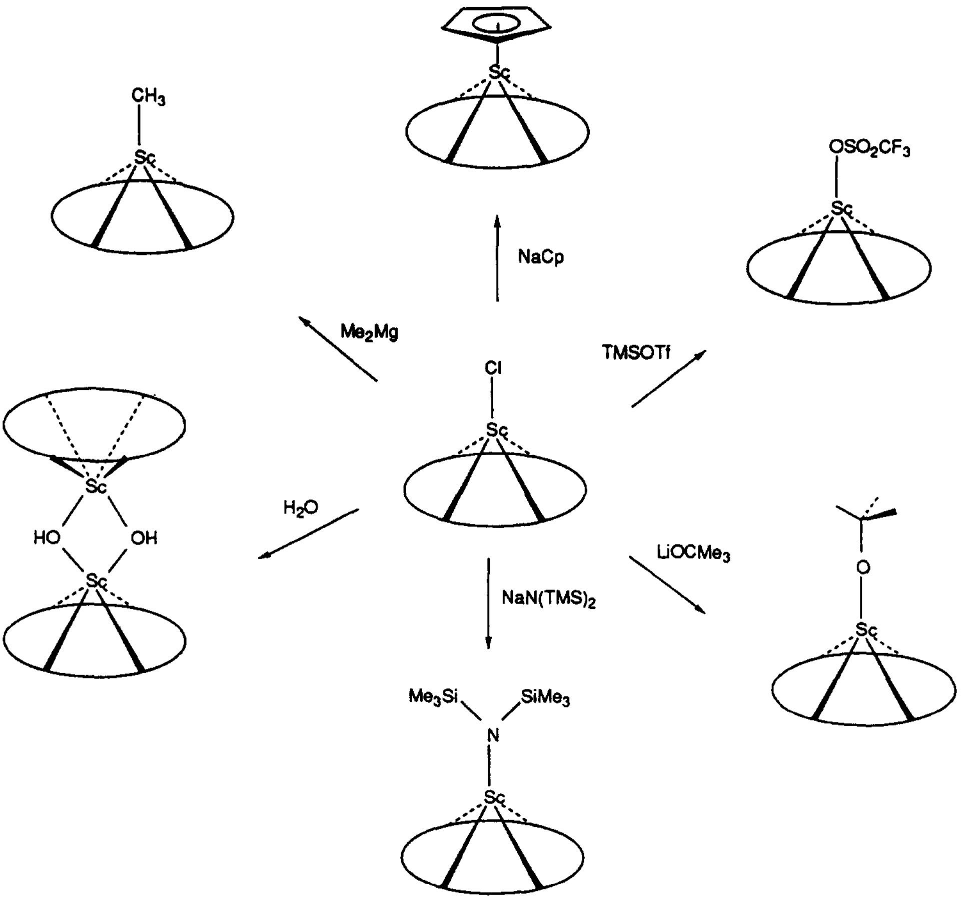
metallic derivatives Sc(OEP)R (R$\equiv$Me, $CH(SiMe_3)_2$, CH_2CMe_3, (η^5-C_5H_5), (η^5-C_9H_7), (η^5-C_5H_4Me), (η^5-C_5Me_5)), see Scheme 3 and Fig. 2.

The alkyl derivative Sc(OEP)Me reacts rapidly with CO_2 and acetone to yield the acetate and butoxide derivatives respectively. Hydrolysis of these derivatives yielded the bridging bis-μ-hydroxide $[Sc(OEP)(\mu\text{-}OH)]_2$, as determined by X-ray crystallography. A related tetraaryl porphyrin complex $[Sc(TpTP)]_2(\mu\text{-}O)$ has been described. This complex is unusual in that it reportedly contains a bent μ-oxide bridge, determined from X-ray diffraction data (Sc–O–Sc 109(3)°) [34].

4. Group 4 metalloporphyrins

4.1. Titanium

Titanium porphyrin derivatives were last reviewed in 1985 [4]. Titanyl mesoporphyrin-IX-dimethyl ester was originally prepared by Tsutsui et al. from the free base porphyrin and 15 equiv diphenyltitanium [35]. Ti(OEP)O was subsequently obtained by reaction of the free base porphyrin with titanocene dichloride [36] or $(acac)_2TiO$ [16] in high boiling solvents. A number of titanyl tetraarylporphyrins were also prepared from free base porphyrin and $TiCl_4$ [37]. The chemical and physical properties of these derivatives were thoroughly investigated. These studies



Scheme 3.

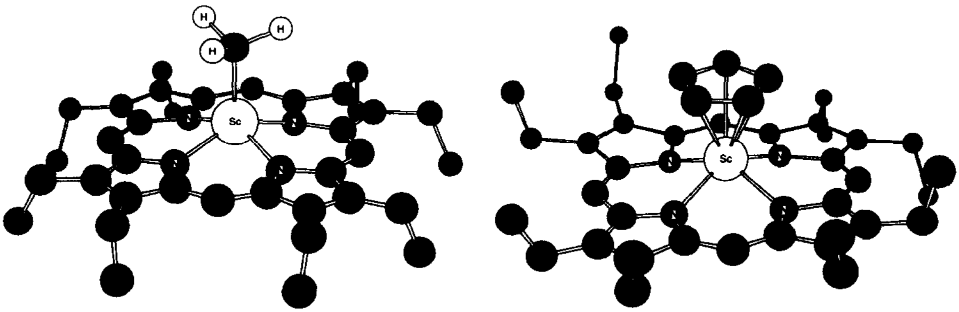


Fig. 2. Crystal structures of Sc(OEP)Me (left) and Sc(OEP)(η^5-C_5H_5) (right) [33].

include electrochemistry [24,37,38], chemical reduction [18,38], rotation of phenyl rings [37,39,40], and electronic properties [27].

The crystal structure of Ti(OEP)O shows the Ti displaced out of the N_4 plane by 0.53 Å and a Ti-oxo bond length of 1.619 Å [41,42], a value identical with the Ti-oxo bond length in the porphodimethene derivative Ti($OEPMe_2$)O [43,44].

The preparation and characterization of a number of peroxotitanium porphyrin derivatives has been reported, including the crystal structure of Ti(OEP)(η^2-O_2) [42,45] and an EXAFS investigation of Ti(TPP)(η^2-O_2) [46]. The dioxygen ligand eclipses two trans nitrogens, a feature which has been explained in terms of overlap of the oxygen π_g-orbital with the metal $3d_{xy}$-orbital [47]. The electrochemistry of these peroxo derivatives has been investigated [42,48]. Reduction takes place initially at the macrocyclic ring, to produce a porphyrin radical anion complex which affords a hydroperoxotitanium(III) porphyrin complex after internal electron transfer and protonation. Subsequent ring reduction and internal transfer of two electrons results in cleavage of the oxygen–oxygen bond to give the oxotitanium(IV) porphyrin and hydroxide. Irradiation of Ti(P)(η^2-O_2)(P≡T*m*TP, TPP) results in the formation of the oxo derivative. A mechanism involving initial generation of a titanium(II) species followed by atom transfer from another peroxo compound has been proposed [49]. The kinetics for the formation of $[\mathrm{Ti(TH_{4py}P)}(\eta^2\text{-}O_2)]^{4+}$ from the titanyl derivative and H_2O_2 has been investigated [50].

Titanium(IV) porphyrins bearing disulfur or diselenium ligands can be prepared from Ti(P)F, or Ti(P)F_2 and $Cp_2Ti(Y_5)$ (Eqs. (5), (6)) [51,52]:

$$\mathrm{Ti(P)F + Cp_2Ti(Y_5) \rightarrow Ti(P)(\eta^2\text{-}Y_2)} \quad (5)$$

$$\mathrm{Ti(P)F_2 + Cp_2Ti(Y_5) \rightarrow Ti(P)(\eta^2\text{-}Y_2)} \quad (6)$$

P≡TPP, T*m*T*p*, T*p*TP, T*p*CF_3PP, TMP, OEP; Y≡S, Se

A crystal structure analysis of Ti(T*p*TP)(η^2-S_2) shows the disulfur ligand to be bound side-on. One-electron electrochemical reduction leads to a stable porphyrin radical anion (cf. the related peroxo derivative above). The second reduction also takes place at the ring, however, the product is unstable [52].

Halide derivatives of titanium porphyrins are prepared easily by reaction of titanyl porphyrins with the corresponding hydrogen halide (Eq. (7)) [53],

$$\mathrm{(P)TiO + HX \rightarrow (P)TiX_2} \quad (7)$$

P≡TPP; X≡F, Cl, Br

The crystal structure of the dibromo derivative shows the two bromides trans to each other with a Ti—Br bond length of 2.454 Å [54]. Similar geometries were also found for the difluoro [55] and dichloro analogs [56] whose mass spectra were also studied in detail [57,58].

Zinc amalgam reduction of Ti(P)F_2 (P≡OEP, TPP) provides entry into low-valent Ti(P)F derivatives [55,59]. EPR spectra show hyperfine interactions with the four equivalent nitrogen atoms and the axial fluorine. Interestingly, electrochemical reduction or chemical reduction with sodium anthracenide generates $[\mathrm{Ti(P)F_2}]^-$ in which both fluorides are still coordinated. In these low valent Ti derivatives the single electron is thought to reside in the metal d_{xy} orbital. Reaction of Ti(TPP)F with dioxygen gives roughly equimolar amounts of Ti(TPP)F_2 and Ti(TPP)(η^2-O_2). Autoxidation of Ti(TPP)(F)(L) (L≡py, 1-MeIm, PBu_3), however, is slower, reflecting the kinetic stabilization by the trans ligand L. A similar study involving autooxidation of Ti(TPP)(SC_6H_5) (prepared from $NaSC_6H_5$ and Ti(TPP)F) resulted in the exclusive formation of Ti(TPP)O and $C_6H_5SSC_6H_5$ [60]. The mechanism proposed involves backside attack of dioxygen to give a peroxotitanium porphyrin derivative and a sulfide radical. The peroxide then reacts with another molecule of Ti(TPP)(SC_6H_5) producing two equivalents of the oxo derivative.

Reaction of Ti(TPP)F with $NaSCH_3$ yields Ti(TPP)(SCH_3) which exchanges the axial ligand on treatment with methanol to afford the corresponding methoxide [61]. An X-ray crystal structure analysis shows a slightly bent methoxide ligand (Ti–O–C 171°) and a Ti–O bond length of 1.77 Å. Treatment of Ti(TPP)F with aryl or benzyl Grignard reagents gives the organometallic derivatives Ti(TPP)R (Eq. (8)) [62],

$$\mathrm{Ti(TPP)F + RMgBr \rightarrow Ti(TPP)R} \qquad (8)$$

$$\mathrm{R \equiv C_6H_6,\ \mathit{o}\text{-}CH_3C_6H_4,\ CH_2C_6H_5}$$

In these organometallic Ti(III) porphyrin derivatives there is no tendency for axial ligation on treatment with potential ligands such as pyridine or *N*-methylimidazole. Reaction with oxygen is rapid, affording the titanylporphyrins and biphenyl in a pathway suggested to be similar to the oxidation of Ti(TPP)(SC_6H_5).

Treatment of Ti(TPP)O with catechol (H_2cat) or 3,4-toluenedithiol (H_2tdt) produces the corresponding chelate complexes Ti(TPP)(cat) and Ti(TPP)(tdt) [63]. Reaction of Ti(TPP)F with Na_2tdt yields [Na][Ti(III)(TPP)(tdt)], where presumably only one sulfur binds to the titanium. Interestingly, electrochemical reduction of Ti(TPP)(tdt) generates the radical anion $[\mathrm{Ti(IV)(TPP^{\cdot})(tdt)}]^-$ bearing a bidentate dithiolato ligand.

Reduction of Ti(P)Cl_2 with $LiAlH_4$ in the presence of diphenylacetylene affords the η^2-alkyne complex shown in Eq. (9) [64]

$$\mathrm{Ti(P)Cl_2 + PhC{\equiv}CPh \xrightarrow{LiAlH_4} Ti(P)(\eta^2\text{-}PhC{\equiv}CPh)} \qquad (9)$$

$$\mathrm{P \equiv OEP,\ T\mathit{p}TP}$$

The crystal structure of this compound shows the phenyl groups bending away approximately 38° from the vector formed by the two alkyne-sp carbons and the titanium is displaced 0.54 Å from the 24-atom porphyrin core. Ti(P)(η^2-Y_2) (P≡T*p*TP, Y≡O; P≡OEP, Y≡S, Se) reacts with Ti(T*p*TP)(η^2-alkyne) (alkyne≡PhC≡CPh, EtC≡CEt) to form the corresponding titanium-oxo, -sulfido, -selenido compounds along with the free alkyne [65]. Treatment of these compounds with Lewis bases such as pyridine or picoline generates the trans-Ti(II) complexes

Ti(T*p*TP)(L)$_2$ (Eq. (10) [66]:

$$\mathrm{Ti(T}p\mathrm{TP)(\eta^2\text{-}PhC{\equiv}CPh) + 2L \rightarrow Ti(T}p\mathrm{TP)(L)_2} \tag{10}$$

$$\mathrm{L \equiv 4\text{-}MeC_5H_4N,\ C_5H_5N}$$

The molecular structure of Ti(T*p*TP)(pic)$_2$ (Fig. 3) shows the Ti sitting in the crystallographically imposed inversion center in a virtually planar porphyrin ring. The two ligands are trans to each other and mutually eclipsed.

Photolysis of titanyl tetraarylporphyrins in the presence of cyclohexane and dioxygen catalytically produces 2-cyclohexen-1-one as the major product along with 2-cyclohexen-1-ol and cyclohexane-1,2-epoxide [67]. Generation of singlet oxygen by the porphyrin compounds has been suggested as a possible mechanism. Ti=O(TPP) catalyzes the epoxidation of cyclohexene and isoprene with ^{t}butylhydroperoxide [68]. A hydroxo(alkylperoxo)(porphyrinato)titanium complex was proposed as the catalytically active species.

4.2. Zirconium and hafnium

Zr(OEP)(OAc)$_2$ was originally prepared by Buchler and coworkers from free-base porphyrin and an excess of Zr(acac)$_4$ in hot phenol, followed by recrystallization from pyridine + glacial acetic acid [16]. The corresponding Hf compound was prepared similarly [17]. The acetate-phenoxide derivative Zr(OEP)(OAc)(OPh) was also isolated from this reaction mixture [69].

The crystal structures of both diacetate compounds have been determined. The

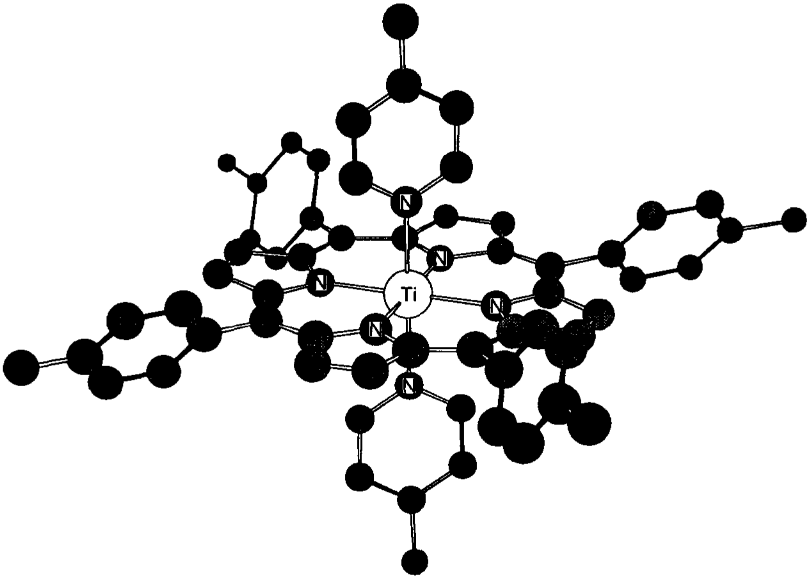


Fig. 3. Crystal structure of Ti(T*p*TP)(4-pic)$_2$ [66].

Hf is displaced 1.01 Å above the N_4-plane by bidentate cis coordinated acetate ligands [70]. Reaction of the Zr and Hf derivatives with excess H(1,3-dion) [$(1,3\text{-dion})^-$ ≡ acetylacetonate, dibenzoylmethanate] afforded the corresponding $M(OEP)(1,3\text{-dion})_2$ complexes, in which the dion ligands are bidentate and cis to each other, as judged by IR and ^1H NMR spectroscopy. The reduction of Zr(OEP)(OAc)(OPh) by sodium anthracenide yields the green porphyrin radical monoanion and, subsequently, the red porphyrin dianion [18,38]. Protonation affords orange–red α,γ-dihydroporphins. The electronic spectra of OEP zirconium(IV) and hafnium(IV) derivatives have been thoroughly studied [27].

Three different methodologies provide entry into zirconium(IV) and hafnium(IV) bis-porphyrinates. Buchler et al. synthesized $M(P)_2$ sandwich compounds (P≡OEP, TTP; M≡Zr, Hf) from $Li_2(P)$ (generated in situ) and Cp_2MCl_2 (Eq. (11) [71,72]. The zirconium sandwich compounds of TPP and OEP have also been prepared from $Zr(NEt_2)_4$ and the free base porphyrin (Eq. (12) [73] and the Zr and Hf bis-OEP have been prepared using the dilithium method (Eq. (13)) [74].

$$2Li_2(P)+Cp_2MCl_2 \rightarrow M(P)_2 \qquad (11)$$

P≡OEP, T*p*TP; M≡Zr, Hf

$$2H_2(P)+Zr(NEt_2)_4 \rightarrow (P)_2Zr \qquad (12)$$

P≡OEP, TPP

$$2Li_2(OEP)\ (THF)_n+MCl_4(THT)_2 \rightarrow M(P)_2 \qquad (13)$$

M≡Zr, Hf

Crystal structures of $Zr(OEP)_2$ [72] and $Zr(TPP)_2$ [71,73] show very short inter-porphyrin distances of 2.531 Å for the former and 2.568 Å for the latter. These sandwich complexes are readily oxidized to afford mono cations [71–74]. The electrochemical, electronic [75] and IR and RR spectroscopic properties are consistent with strong π–π interactions between the two porphyrin rings.

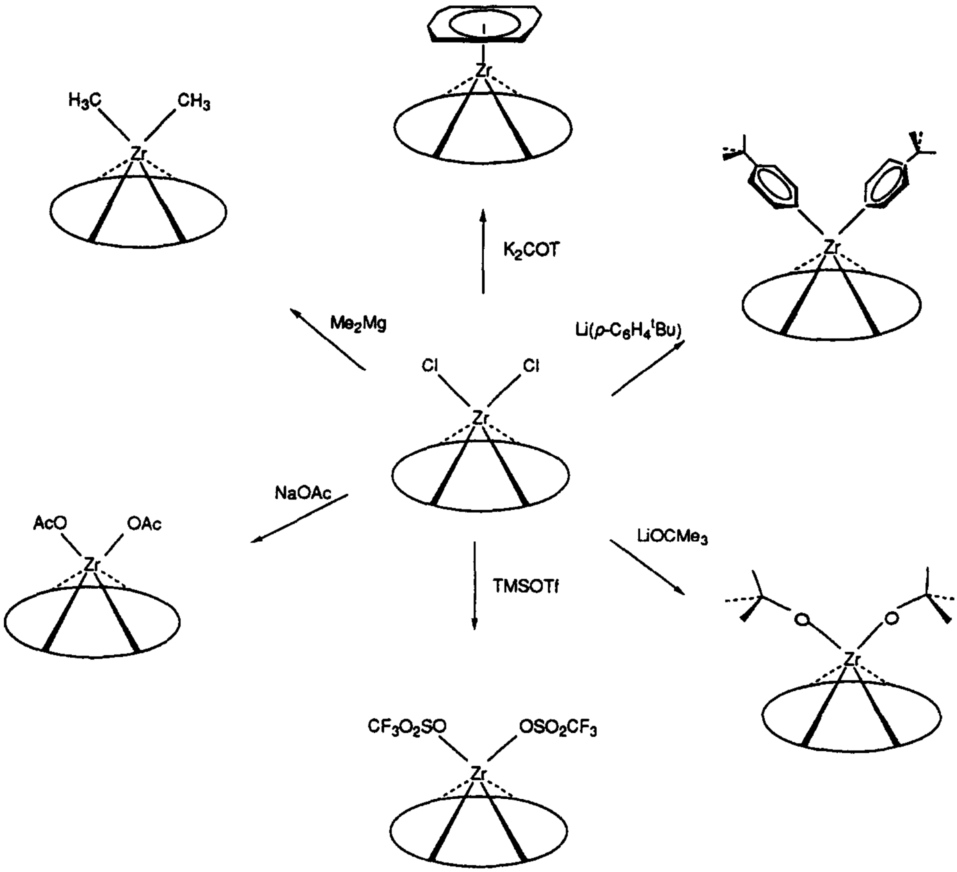
Pseudo-sandwich complexes of the type M(P)(Schiff-base-dianion) are accessible from $M(P)(acac)_2$ and Li_2(Schiff-base) (M≡Zr, Hf; P≡OEP, TPP; Schiff-base-dianion ≡ $(salen)^{2-}$, $(3\text{-MeO-salen})^{2-}$, $(3,5\text{-}Cl_2\text{-salen})^{2-}$, $(5\text{-}O_2N\text{-salen})^{2-}$, $(salophen)^{2-}$) [31].

$Zr(TPP)Cl_2$ was first isolated by Berezin and Lornova from free-base porphyrin and $ZrCl_4$ in benzonitrile after chromatography and treatment with HCl [76]. A high yield, large scale procedure to produce $Zr(OEP)Cl_2$ using the dilithium methodology was recently described (Eq. (14)) [77,78].

$$Li_2(OEP)(DME)_n+ZrCl_4(DME) \rightarrow Zr(OEP)Cl_2 \qquad (14)$$

$Zr(OEP)Cl_2$ serves as a useful synthon for further functionalization. Alkyl, aryl, alkoxide, acetate, triflate, carborane and cyclooctane derivatives have been obtained [77,78] (Scheme 4) [79].

The crystal structures of $Zr(OEP)Cl_2$, $Zr(OEP)(O^tBu)_2$, $Zr(OEP)Me_2$, and



Scheme 4.

Zr(OEP)(CH$_2$SiMe$_3$)$_2$ have been reported (Fig. 4). In general, with the exception of the di-*tert*-butoxide derivative, the metal is displaced ca. 0.9 Å out of the N$_4$-plane and the X–Zr–X angle is approximately 80° (see below).

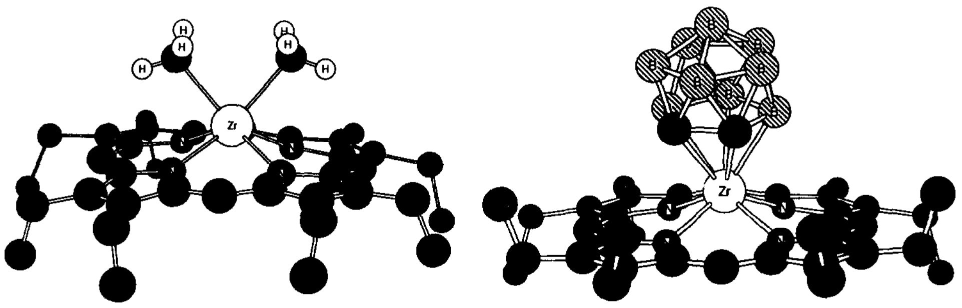


Fig. 4. Crystal structures of Zr(OEP)Me$_2$ (left) and Zr(OEP)(B$_9$C$_2$H$_{11}$) (right) [78,79].

Alkyl derivatives of Zr and Hf porphyrins can also be obtained directly on large scales from the dilithium porphyrins and dialkylmetal dichlorides (generated in situ) in almost quantitative yields (Eq. (15)).

$$\mathrm{Li_2(P)(THF)}_n + \mathrm{(Me_3SiCH_2)_2MCl_2} \rightarrow \mathrm{Zr(P)(CH_2SiMe_3)_2} \qquad (15)$$

$$\mathrm{P} \equiv \mathrm{T}p\mathrm{TP, OEP;\ M} \equiv \mathrm{Zr, Hf}$$

The alkyl derivatives are particularly reactive toward small unsaturated molecules. Whereas reaction of dialkyl(octaethylporphyrinato)-zirconium with CO or isonitriles leads to the formation of a number of complex mixtures, reactions with CO_2 and acetone cleanly yield the insertion products $Zr(OEP)(OAc)_2$ and $Zr(OEP)(O^tBu)_2$ respectively (Scheme 5) [77,78]. It could be shown that, in contrast to late transition metal and main group porphyrins, radicals are not involved in these reactivities.

Reaction of $Zr(OEP)(CH_2SiMe_3)_2$ with dihydrogen produces TMS and $Zr(OEP)CH_2SiMe_3$, in which the metal is formally in the oxidation state 3+ [80]:

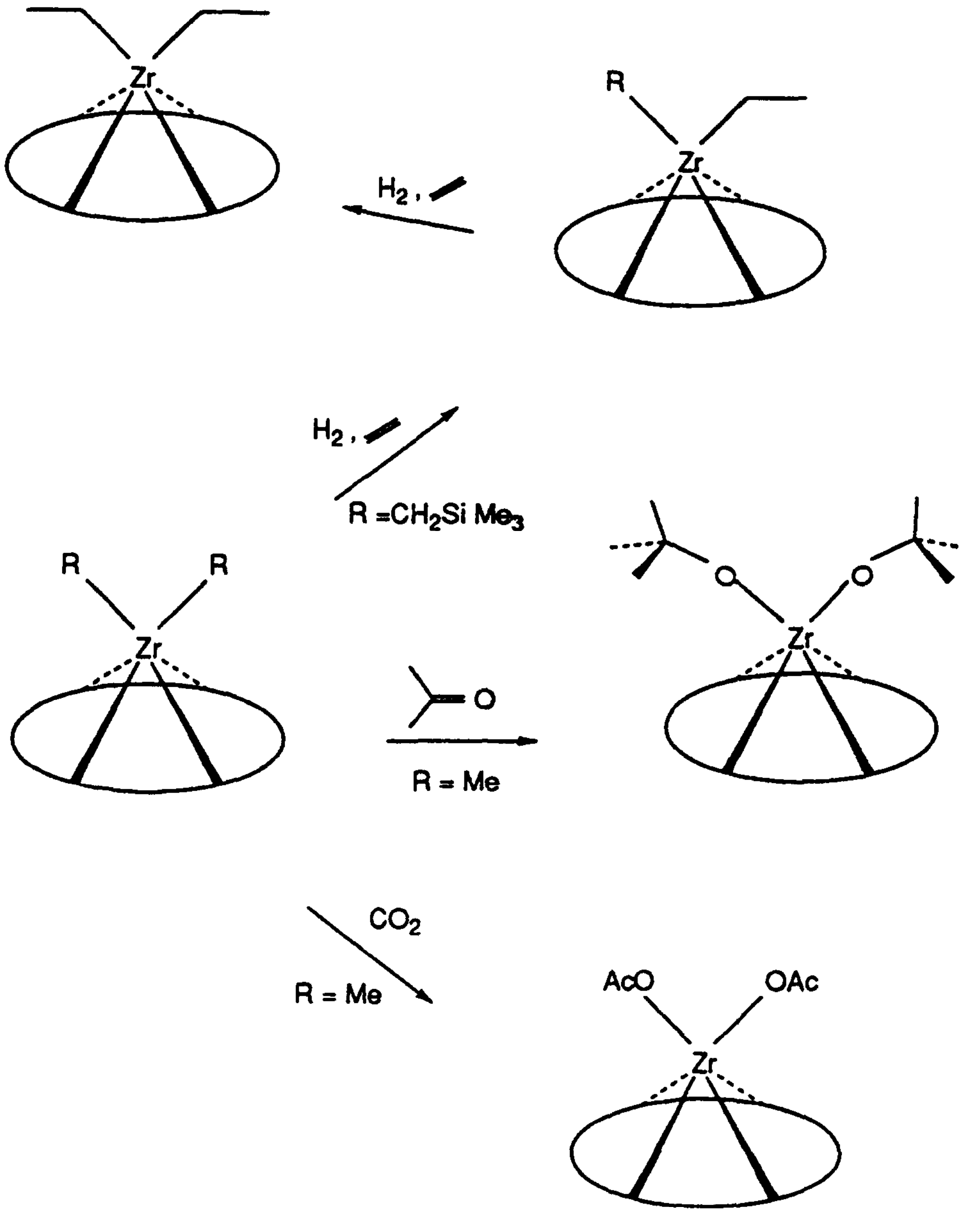
$$\mathrm{Zr(OEP)(CH_2SiMe_3)_2} + \mathrm{H_2} \rightarrow \mathrm{Zr(OEP)CH_2SiMe_3} + \mathrm{TMS} \qquad (16)$$

X-ray crystallography and ^1H NMR, EPR, and UV–visible spectroscopy show that this compound is best viewed as a resonance hybrid between two limiting structures, one involving a Zr(IV) porphyrin radical anion and the other a Zr(III) alkyl porphyrin (Fig. 5).

The Zr(IV) dialkyls act as precatalysts for the catalytic hydrogenation of 1-alkenes such as ethylene, propene, or 1-hexene [77]. The putative Zr hydride intermediate was not observed directly, but its participation could be inferred from deuterium labeling experiments.

Kim and coworkers have also used the dilithium method to prepare $Zr(OEP)Cl_2$ and $Zr(TPP)Cl_2$ [81] as well as the corresponding hafnium derivatives [82]. Functionalization of $Zr(TpTP)Cl_2$ afforded the corresponding dimethyl derivative, and the carborane $Zr(OEP)(\eta^5\text{-}C_2B_9H_{11})$ was also obtained [81]. The crystal structure of $Zr(TPP)Cl_2(THF)$, crystallized in the presence of a large excess of THF, was determined; in contrast to $Zr(OEP)Cl_2$, this compound is seven coordinate although the donor ligand was determined to be labile in solution. Similarly $Hf(OEP)Cl_2$ crystallized with an additional ligand (H_2O in this case) giving a similar coordination geometry around the metal. Seven coordination was also observed in the structures of $Hf(OEP)(P_3O_9)$ [82], and the oxygen and hydroxo bridged zirconium dimers, $(\mu\text{-OH})_3[Zr(OEP)]_2(7,8\text{-}C_2B_9H_{12})$ and $(\mu\text{-O})(\mu\text{-OH})_2[Zr(TPP)]_2$ [83].

Reaction of acetate and related derivatives of Zr(TPP) (prepared by a method analogous to the preparation of $Zr(OEP)(OAc)_2$) with HCl also generates the dichloride [84]. These Zr(TPP) derivatives serve as efficient catalysts for the ethylalumination of alkynes. The acetate derivative can be functionalized with alkyl lithium or Grignard reagents to yield $Zr(TPP)R_2$ ($R \equiv$ Me, Et, ^{n}Bu, Ph). Photolysis of the dimethyl derivative was reported to produce a zirconium(II) porphyrin compound [85]. The authors suggest a structure in which the zirconium is sitting in the plane of the porphyrin ring, with two diethyl ether ligands trans to each other. Remarkably, the compound is reported to be diamagnetic and readily



Scheme 5.

demetallated on addition of water. One would expect such a compound to be paramagnetic (compare with the high spin d^3 (TPP)V(THF)$_2$ compound and others) [86,87] and furthermore it is not clear why this derivative should be demetallated on addition of water.

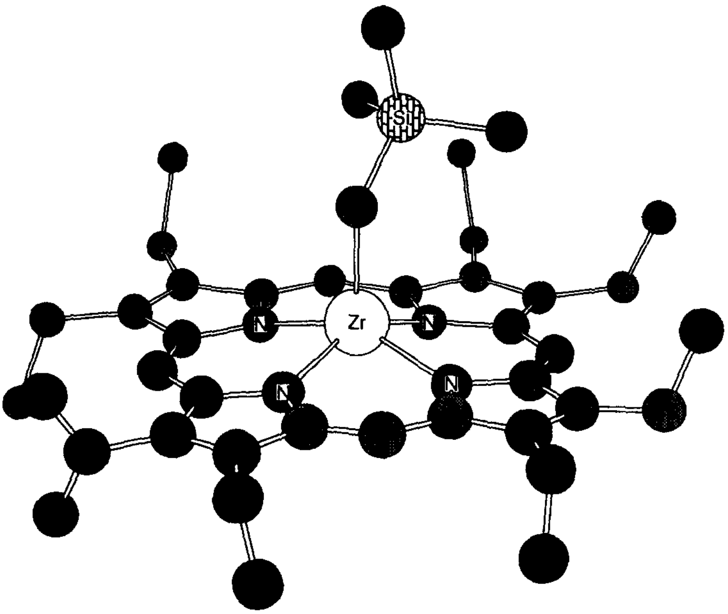


Fig. 5. Crystal structure of Zr(OEP)(CH_2SiMe_3) [80].

5. Group 5 metalloporphyrins

5.1. Vanadium

Vanadium porphyrin compounds were reviewed recently [4]. The first vanadium porphyrin compound V≡O(DPEP) was isolated by Treibs [88,89], who also prepared the first synthetic porphyrin (V=O(*meso*-DME)) [90]. There is a wide range of synthetic entries into vanadyl porphyrins using a variety of metal starting materials such as vanadyl acetate [16,91], vanadium hexacarbonyl [35,92], divalent vanadium salts [93], vanadium trichloride [94], vanadium tetrachloride, vanadyl dichloride or vanadyl sulfate [95,96].

The crystal structures of V=O(DPEP) [97,98] and V=O(OEP) [99] have been determined and ^1H and ^{14}N ENDOR has been used to investigate V=O(TPP) [100,101]. Numerous studies have been devoted to elucidate the chemical and physical properties of vanadyl porphyrins. EXAFS has been used to probe the vanadium chemical environment in asphaltanes [102] and EPR was used to identify vanadyl porphyrins deposited on Al_2O_3 [103]. The aggregation of vanadyl porphyrins was investigated by IR [104] and by a variety of electrochemical and spectral methods such as UV–visible EPR and NMR [105]. The dimerization of crown ether derivatives of tetraarylporphyrins was probed by a combination of UV–visible and EPR spectral methods [106]. The electrochemical [24,107] and chemical reduction by sodium anthracide has been reported [18,38], and further functionalization to form porphodimethenes [43] has been studied. As with the group 4 metal porphyrins, the vanadylporphyrins can be reduced to the green monoanion and subsequently to the red dianion. Protonation initially affords the α,γ-dihydroporphin derivative which thermally rearranges to the chlorin. Ligands trans to the vanadyl-oxo moiety are labile [96] and the Hammett σ,ρ relationship between the exchange rate and phenyl para-substituents in tetraarylporphyrins has been probed [108]. Binding of the vanadyl (*meso*-tetrakis(4-*N*-methylpyridinium)porphyrin) to DNA has been investigated in light of possible medical applications of porphyrins [109]. One study addressed thermodynamics in the hydrogenation of the porphyrin moiety in vanadyl octaethylporphyrin [110].

Effects of solvents and axial ligation on the V=O stretching Raman frequency was studied [86] and the force constant calculated [87]. Electrochemical oxidation of vanadylporphyrins (OEP, TPP, TMP) yields the porphyrin radical cation as shown by RR measurements [86,111]. For the tetraarylporphyrin derivatives, this electron is removed from the a_{2u} orbital. Since in out-of-plane metal porphyrins mixing between this ligand and the metal d_{z^2} is possible, electron density is removed from the metal–oxygen bond. This bond weakening has obvious implications for the understanding of cytochrome P-450 models, since porphyrin radical cations have been proposed as intermediates in oxidation reactions. V=O(TPP) has been shown to catalytically oxygenate cyclohexene in the presence of oxygen under photolytic conditions [67]. The X-ray crystal structures of V(T*p*TP)O, V(ETP)O and an 1,4-dihydroxybenzene adduct of (ETP)VO have been determined. The V–O bond distances are 1.625(16) Å, 1.599(6) Å and 1.614(9) Å with the metal 0.53 Å, 0.49 Å and 0.51 Å out of plane [112].

$V(P)Cl_2$ (P≡OEP, TPP, T*m*TP, T*p*TP) were prepared from the vanadyl species and thionylchloride or oxalylchloride [113]. Exchange of the halide ligand with excess HBr afforded the corresponding dibromides. An EXAFS study of $V(OEP)Br_2$ deduced the trans nature of the halides and the lack of an EPR signal for this d^1 compound was explained by an orbitally degenerate ground state by an INDO/S molecular orbital calculation. Organylimido vanadium porphyrins were prepared by treatment of $V(P)Cl_2$ with the corresponding amine [94] including a cationic alkylamido vanadium(V) species [114].

$V^{II}(P)(L)_2$ derivatives (P≡OEP, TPP, T*m*TP, T*p*TP, L≡THF, $PPhMe_2$) have been obtained by zinc amalgam reduction of the dihalides. The X-ray crystal structures of the V(OEP) derivatives with L≡THF and $PPhMe_2$ have been determined [115,116]. The ligands are trans to each other, a remarkable finding considering the ionic radius of hexacoordinated vanadium is 0.79 Å [117].

These low valent vanadium derivatives serve as convenient synthons for further functionalization. Reaction of the THF derivatives with elemental sulfur or Cp_2TiSe_5 affords the thio and seleno compounds (Eq. (17) [118,119]

$$V(P)(THF)_2 + Cp_2TiSe_5 \rightarrow V{=}Se(P) \qquad (17)$$

5.2. Niobium and tantalum

The chemistry of niobium porphyrin complexes was recently reviewed [8]. Reaction of MCl_5 (M≡Nb, Ta) with $H_2(OEP)$ affords $M(OEP)F_3$ after treatment with aqueous HF [17]. A cis arrangement of the three fluorides was proposed. Aqueous work-up of the crude products of the reaction of $NbCl_5$ with various free base porphyrins generates $[Nb(P)]_2O_3$ species (P≡OEP, OMP, TPP, T*p*TP) [120,121]. Recrystallization of the latter from acetic acid produces Nb(P)(O)(OAc). Similarly, treatment of the reaction mixture with HCl generates $Nb(TPP)Cl_3$ [76]. A further entry into trihalide derivatives involves treatment of $[Nb(TPP)]_2O_3$ with HCl or HBr [122]. In a similar vein, reaction of $[Nb(TPP)]_2O_3$ with acetyl acetonate produces Nb(TPP)(O)(acac). A series of Nb(V) and Ta(V) complexes containing tetraarylporphyrinato ligands including $[Ta(TPP)]_2O_3$ has been prepared [123].

As deduced by X-ray crystallography, the Nb is seven coordinate in $[Nb(TPP)]_2O_3{\cdot}CHCl_3$ with three bridging oxygen ligands [124,125]. The Nb is displaced 1.02 Å out of the plane of the N_4 plane, but the Nb–O distances of each unique niobium atom are significantly different. One oxygen atom forms a nearly symmetrical bridge between the two niobium atoms, whereas each of the other oxygen atoms is more closely associated with a different Nb atom. Remarkably, the Nb–O bond distances in the identical complex crystallized with a molecule of dichloroethane in the lattice, $[Nb(TPP)]_2O_3{\cdot}C_2H_4Cl_2$, are essentially equal [121]. X-ray crystal structure analyses of Nb(TPP)(O)(OAc) [121,126] and Nb(OEP)(O)F [127] (Fig. 6) also show cis coordination about the metal.

Reduction of Nb(P)(O)(OAc) (P≡OEP, TPP, T*p*TP) by Zn/Hg leads to the Nb(IV) oxo Nb–O(P) [128,129]. Similar treatment of $Nb(P)X_3$ (P≡TPP, T*p*TP; X≡Cl, Br) forms $Nb(P)X_2$ [14,129]. EPR data indicate a trans species with the single unpaired electron in the d_{xy} orbital. Exposure of this compound to O_2 generates a species with EPR features indicative of an Nb(V) superoxide complex. The physical and chemical properties of these Nb(IV) and Nb(V) compounds have been studied including the electronic spectra [27] and electrochemistry [130–132]. The photoredox behavior of $[Nb(TpTP)]_2O_3$ and photochemical epoxidation of olefins with molecular oxygen catalyzed by $[Nb(TpTP)]_2O_3$ and photochemical epoxidation of olefins with molecular oxygen catalyzed by $[Nb(TpTP)]_2O_3$ has been reported [133,134].

The ligands in the six- and seven-coordinate Nb(V) compounds are cis, whereas a trans geometry is found for the Nb(V) dihalides. Given that ionic radii for six- and seven-coordinate Nb(V) are 0.64 and 0.69 Å respectively, and that the value for hexacoordinate Nb(IV) is 0.68 Å, these results illustrate that accurate predictions of

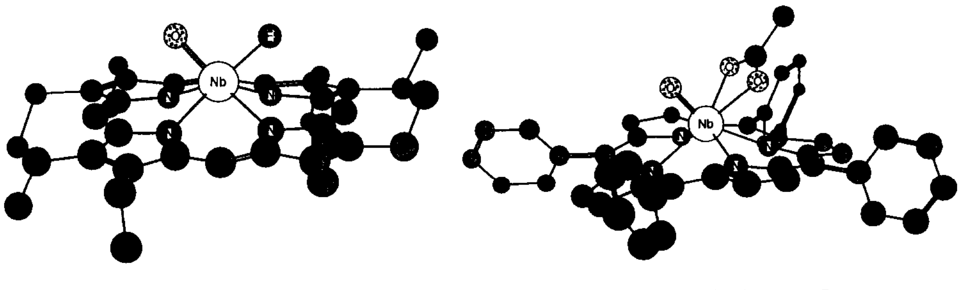


Fig. 6. Crystal structures of Nb(OEP)(O)F and Nb(TPP)(O)OAc [126,127].

cis or trans geometries in related complexes cannot be based solely on considerations of ionic radius [117].

6. Group 6 metalloporphyrins

6.1. Chromium

The first chromium porphyrin compound Cr(*meso*-DME) was prepared by Tsutsui and co-workers from the free base porphyrin and $Cr(CO)_6$ in hot *n*-decane [92,135]. Use of various alcohols as eluents during chromatography of these divalent species generated the corresponding alkoxide derivative [136]. The synthesis of Cr(TPP)Cl from $CrCl_2$ and H_2(TPP) in boiling DMF was reported shortly thereafter [93]. Cr(T*p*TP)Cl was prepared employing the same methodology and metathesis reactions with NaN_3 or NaI in CH_2Cl_2 afforded the chromium iodide and azide compounds [136]. Reaction of Cr(TPP)Cl with HBr gave Cr(TPP)Br [137]. A report on the preparation of $Cr(TPP)(CO)_3$ has appeared, but the nature of the compound isolated remains suspicious [138]. Two entries into Cr(OEP)(OPh) have been reported, the first involves heating trivalent chromium chloride in benzonitrile at 195 °C and recrystallization from phenol + methylene-chloride + toluene [17]. Alternatively, the compound can be generated directly from H_2(OEP) and $Cr(acac)_3$ in hot phenol [18].

The crystal structures of Cr(TPP)·2Tol [139] and $Cr(TPP)(py)_2$ [140,141] have appeared. The interesting feature about the first structure is the close contact of one toluene solvate with the metal porphyrin, suggesting a π–π interaction. Investigation of the physical properties of chromium(III) porphyrins includes measurement of the absorptions and luminescence [142], paramagnetic NMR [143,144], and EPR spectra of spin-labeled pyridines coordinated to Cr(TPP)Cl [145]. Cr(TPP)Cl and Cr(II) derivatives coordinate bases with O-, S-, N- or P-donor groups, which exchange under the appropriate conditions [137,146–150].

The photochemistry of chromium porphyrins has been reviewed [151] and the redox properties of chromium porphyrin derivatives have been thoroughly probed [24,152–156]. The site of initial reduction depends on the electron affinity of the porphyrin ligand and of the electron-donor properties of the axial ligands. Strongly electron-donating ligands such as pyridine or DMSO promote ligand reduction [156]. Reduction of Cr(OEP)(OPh) with sodium anthracenide gives first the mono-anion and then the dianion, which can be alkylated by methyl iodide to the porphodimethene [18,38].

Chromium(II) porphyrins react with oxygen to form chromium(III) species which can be further oxidized to oxochromium compounds [157–159]. Cr(TPP)Cl can be converted to a chromium(V) compound by treatment with iodosylbenzene or *m*-chloroperoxybenzoic acid [160], or using *p*-cyano-*N*,*N*-dimethyl-aniline N-oxide under photolytic conditions [161]. The oxidized species was identified by UV–visible IR, EPR, and magnetic susceptibility, with the data suggesting the presence of a Cr(V)=O moiety [160,162]. Alkenes are epoxidized and alcohols are oxidized to aldehydes by this species [160]. The oxochromium(V) compound decomposes to the stable Cr(IV) complex Cr=O(TPP) [163].

Oxo complexes Cr=O(P) (P≡TPP, T*p*TP, TMP, OEP) are accessible from the corresponding chlorides and iodosylbenzene, *tert*-butylhydroperoxide followed by KOH, by treatment with sodium hypochlorite [163,164], or by auto-oxidation of Cr(TPP) [165]. The crystal structure of Cr=O(TPP) shows a Cr–O bond length of 1.572 Å with the Cr displaced 0.469 Å out of the N_4 plane [163,165]. In the series M=O(P), where M≡V, Cr, Mn, Fe, the chromium complex has the largest M=O force constant [87].

Oxochromium(IV) and (V) compounds display a rich oxygenation chemistry. It has been shown that oxochromium(V) compounds react in a two-electron reaction to oxidize *t*-butylphenylcarbinol to the ketone, whereas oxochromium(IV) derivatives undergo a one-electron oxidation resulting in the cleavage of *t*-butylphenylcarbinol to yield benzaldehyde [166]. Epoxidation of alkenes by oxochromium(V) compounds has been the subject of several studies [167–171]. Other oxidation reactions involve hydrogen abstractions from hydrocarbons to form alcohols by chromium porphyrins and a variety of oxidation reagents [172–175]. The oxygenation chemistry of metalloporphyrins has been reviewed recently [10,11].

Oxygen atom transfer from a variety of peracids and hydroperoxides has been studied [176]. Chromyl porphyrins react with M(L) compounds, (M≡V, Cr, Mo, Fe etc.; L≡porphyrin, phthalocyanine, Schiff-base) to give oxygen bridged dimers Cr(P)OM(L) [158,159,177,178]. Oxygen transfer between Cr=O(P) and Cr(P)Cl (P≡OEP, TPP) [179] and the atom transfer reaction between Mn(OEP)N and Cr(TPP)Cl has been studied [180]. Woo has recently reviewed the topic of atom transfer reactions [12].

Nitridochromium(V) porphyrins were prepared by hypochlorite oxidation of Cr(P)Cl (P≡TPP, OEP) in the presence of ammonia [181] and by photolysis of chromium(III) azides [182,183]. An X-ray crystal structure determination shows Cr≡N(T*p*TP) to be isostructural with the oxo compound, with a Cr–N bond distance of 1.565 Å and the Cr displaced 0.42 Å above the mean plane of the pyrrole nitrogens [182]. The polarized X-ray absorption near-edge spectra for Cr=O(T*p*TP) and Cr≡N(T*p*TP) have been reported [184].

Metathesis reactions of Cr(T*p*TP)Cl and organolithium or Grignard reagents affords Cr(T*p*TP)R (R≡C_6H_5, p-$^t BuC_6H_4$, CH_2SiMe_3) (Eq. (18)) [185]

$$\mathrm{Cr(T}p\mathrm{TP)Cl} + \mathrm{LiCH_2SiMe_3} \rightarrow \mathrm{Cr(T}p\mathrm{TP)CH_2SiMe_3} \qquad (18)$$

Reaction of these organometallic derivatives with oxygen in chlorinated solvents generates the Cr=O(T*p*TP) derivative, presumably via backside attack of the oxygen onto the Cr(III) alkyl followed by homolysis of the Cr–R bond to give Cr(T*p*TP)(O_2); this species then combines with another chromium(III) compound to afford the oxo derivative.

6.2. Molybdenum and tungsten

Molybdenum and tungsten porphyrin compounds are known for oxidation states II–VI, although the metal(V) derivatives are the most thoroughly studied.

Mo(TPP)(O)(X) (X≡OH, Cl, OOH, OEt) were prepared in a similar manner to the Cr homologues, i.e. from the free base porphyrin and $Mo(CO)_6$ in hot decalin [136,186]. Other entries into M(P)(O)(X) (P≡OEP, TPP etc., X≡Cl, OMe, OEt) derivatives include heating the free base porphyrin in high boiling solvents such as phenol or benzonitrile with metal salts such as WF_5, H_2WO_4, $K_3W_2Cl_9$, $Mo(acac)_3$, or $MoCl_2$, $Mo(O)Cl_3$ [16,17,187,188] or reaction of the free base porphyrin with $MoCl_5$ in hot decalin in the presence of NaOAc [189].

A reinvestigation of the hydroxide compound described by Fleischer actually showed it to be the dimer $[Mo(TPP)(O)]_2O$ [124,125]. The hydroxo compound can, nevertheless, be prepared from Mo(TPP)(O)Cl and NaOH in CH_2Cl_2 [190]. An oxomolybdenum corrole compound was prepared using similar methodology to that described above for Mo(TPP)(O)X [191].

The ethoxide ligand in Mo(TPP)(O)(OEt) could be easily exchanged by treatment with sodium or potassium salts NaX (X≡Cl, Br, NCS) in CH_2Cl_2 [192]. The crystal structures of Mo(TPP)(O)Cl [193], $[Mo(TPP)(O)]_2O$ [124,125], and $[Mo(OEP)(O)]_2O$ [194] have been determined and in all derivatives the terminal oxide is trans to the chloride or bridging oxide respectively. The $Mo—O_{terminal}$ bond length in both compounds is effectively the same, i.e. 1.714(3) Å for the chloride, 1.707(3) Å and 1.721(6) Å for the bridging species. Other molybdenum oxo porphyrins studied by X-ray crystallography include Mo(TPP)O(NCS) [195], Mo(TPP)O(F) [195], and (5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrinato) oxomolybdenum methoxide [196]. The nitrido complex $[Mo{\equiv}N(TPP)]Br_3$ has been reported [197].

Various oxomolybdenum(V) and oxotungsten(V) species have been studied by absorption spectroscopy [198–200], ESR [199,201], RR [202] and electrochemistry [15,24,105,203,204]. Chemical reduction with sodium anthracenide affords first the mono-anion and then the dianion, which can be functionalized to porphodimethenes [18,38]. The chemical reactivity of these derivatives has been thoroughly probed and the oxidation chemistry has been reviewed recently [8]. The reaction of oxomolybdenum(V) compounds with superoxide [205–207] and their photochemical reduction has been studied [208]. In the presence of a catalytic amount of oxo(porphyrinato)molybdenum(V) compounds, alkenes are epoxidized by hydrogen peroxide [209,210] or ᵗbutylhydroperoxide [211]. The photo-assisted epoxidation of alkenes [212] and the reduction of molecular oxygen to hydrogen peroxide catalyzed by molybdenum(V) porphyrins [213] has been reported.

Reaction of Mo(T*p*TP)(O)(OH) with hydrogenperoxide in CH_2Cl_2 affords *trans*-$Mo(TpTP)(\eta^2-O_2)_2$. An X-ray crystallographic analysis shows the peroxo ligands side-on and mutually staggered, eclipsing the Mo—N bonds [214]. The physical and chemical properties of this compound have been subject to a recent study [215]. Diperoxomolybdenum(VI) porphyrin is thermally stable; however, photolysis results in the formation of dioxygen and *cis*-dioxo-molybdenum(VI) porphyrin (Eq. (19), Fig. 7) [216]

$$trans\text{-}Mo(TpTP)(\eta^2\text{-}O_2)_2 \xrightarrow{h\nu} cis\text{-}Mo(TpTP)(O)_2 \qquad (19)$$

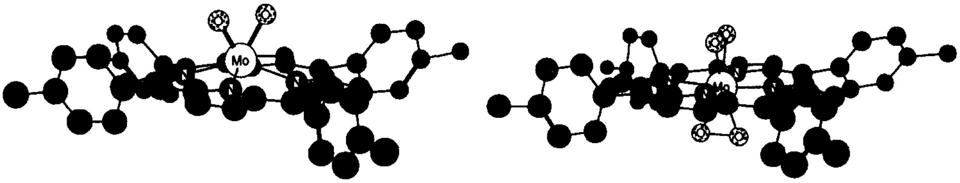


Fig. 7. Crystal structures of Mo(T*p*TP)(O)$_2$ (left) and Mo(T*p*TP)(η^2-O$_2$)$_2$ (right) [216,214].

The crystal structure shows Mo—O bond lengths of 1.709(9) Å and 1.744(9) Å and an O—O distance of 2.547(13) Å, which is much longer than a peroxide bond length. The O—O vector is eclipsed with respect to the four pyrrole nitrogen atoms, which was explained in terms of possible oxygen–nitrogen repulsive interactions [217]. Using a similar methodology (5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrinato) cis dioxomolybdenum was prepared [196]. Reaction of W(TPP) starting materials with H_2O_2 produces the cis oxo-peroxo derivative [218]. The reactions of tungsten porphyrins with H_2O_2 have been studied in detail [219]. The crystal structure shows an unusual geometry with the central metal 1.49 Å above the N_4 plane of a severely distorted porphyrin ring. Hexacoordinate W(VI) has an ionic radius of 0.59 Å [117], clearly small enough to fit into the porphyrin plane, yet a relatively stable cis coordinated compound is obtained.

Cis-Mo(T*p*TP)(O)$_2$ oxidizes isopropanol to acetone by two one-electron pathways via Mo(V) species [220], and tertiary phosphines to phosphine oxides via Mo(IV) compounds [221]. The electrochemical activation of the Mo–oxo bond has been probed [222]. Mo(IV) derivatives were originally prepared by reduction of Mo(TPP)(O)(OH) with hydrazine [136] or directly by reaction of H$_2$(OEP) with Mo(acac)$_3$ in hot phenol [16] to afford Mo=O(P) (P≡TPP, OEP). Entries into M(P)Cl$_2$ (P≡OEP, T*p*TP; M≡Mo, W) include heating Mo=O with trimethylsilylchloride or reduction of W(P)(O)(Cl) with Si$_2$Cl$_6$ [223,224]. The reversible reaction of Mo(IV) derivatives with dioxygen has been reported [225]. Mo(P)Cl$_2$ (P≡OEP, T*p*TP) was prepared from the corresponding oxo derivatives by treatment with HCl [226]. The crystal structure of the tetraaryl compound established the trans arrangement of the two halide ligands with Mo—Cl bond lengths of 2.347(4) Å and 2.276(4) Å.

Zinc amalgam reduction of Mo(T*p*TP)(O)(Cl) also affords the Mo(IV) oxo compound which could then be converted to the dichloro derivative by treatment with HCl [227]. Functionalization of Mo(T*p*TP)Cl$_2$ with *N*-phenylhydroxylamine afforded the bridging μ-oxo derivative [Mo(T*p*TP)Cl]$_2$O [228], and reaction with phenylhydrazine resulted in the formation of a *trans*-bis(phenyldiazo) compound [229]. The molecular structure of both compounds was established by X-ray crystallography. Only one organometallic Mo porphyrin compound Mo(TPP)Ph)(Cl) is known, obtained serendipitously during an attempt to recrystallize Mo(TPP)(CO)$_2$ (see below) [230]. The Mo—C and Mo—Cl bond lengths are 2.241(4) Å and 2.382(1) Å as established by X-ray crystallography.

Reduction of $Mo(TpTP)Cl_2$ with zinc amalgam under an atmosphere of NO results in the formation of *cis*-$Mo(TpTP)(NO)_2$ (Eq. (20)). Traces of methanol in the eluent during chromatography produces the *trans*-Mo(TpTP)(NO)(MeOH) (Eq. (21)).

$$Mo(TpTP)Cl_2 + 2NO \xrightarrow{Zn/Hg} cis\text{-}Mo(TpTP)(NO)_2 \tag{20}$$

$$cis\text{-}Mo(TpTP)(NO)_2 + MeOH \rightarrow trans\text{-}Mo(TpTP)(NO)(MeOH) \tag{21}$$

In *cis*-$Mo(TpTP)(NO)_2$ the Mo is displaced 0.99 Å out of the porphyrin plane with a mean Mo–N(NO) bond distance of 1.70(1) Å and an N(NO)–Mo–N(NO) bond angle of 78.4(5)°. The crystal structure of *trans*-Mo(TpTP)(NO)(MeOH) shows a longer Mo–N(NO) bond distance of 1.746(6) Å [231].

Treatment of $Mo(TpTP)Cl_2$ with an excess of $LiAlH_4$ in toluene in the presence of diphenyl acetylene generates Mo(TpTP)(η^2-PhC≡CPh) (Eq. (22)) [232]

$$Mo(TpTP)Cl_2 + PhC{\equiv}CPh \xrightarrow{LiAlH_4} Mo(TpTP)(\eta^2\text{-}PhC{\equiv}CPh) \tag{22}$$

The Mo in this compound is displaced 0.63 Å out of the N_4 plane and the acetylene ligand acts as a four-electron donor as judged by the short Mo–C(sp) bond length of 1.974(4) Å. Similar methodologies have been used to prepare other M(P) (η^2-PhC≡CPh) compounds (P≡OEP, TpTP; M≡Mo, W) [223,224]. Reduction of $Mo(TpTP)Cl_2$ with Zn/Hg under an atmosphere of CO generates *cis*-$Mo(TpTP)(CO)_2$ (Eq. (23)), which can be converted to *trans*-$Mo(TpTP)(py)_2$ with an excess of pyridine (Eq. (24)) [233].

$$Mo(TpTP)Cl_2 + 2CO \xrightarrow{Zn/Hg} cis\text{-}Mo(TpTP)(CO)_2 \tag{23}$$

$$cis\text{-}Mo(TpTP)(CO)_2 + 2py \rightarrow trans\text{-}Mo(TpTP)(py)_2 \tag{24}$$

The crystal structures of both compounds confirm the geometry about the metal (Fig. 8).

Reduction of $W(OEP)Cl_2$ with Al/Hg in refluxing PEt_3 affords *trans*-$W(OEP)(PEt_3)_2$ as judged by ^1H NMR [224].

A variety of porphyrin dimers with multiple M–M bonds $[M(P)]_2$ (M≡Mo, W;

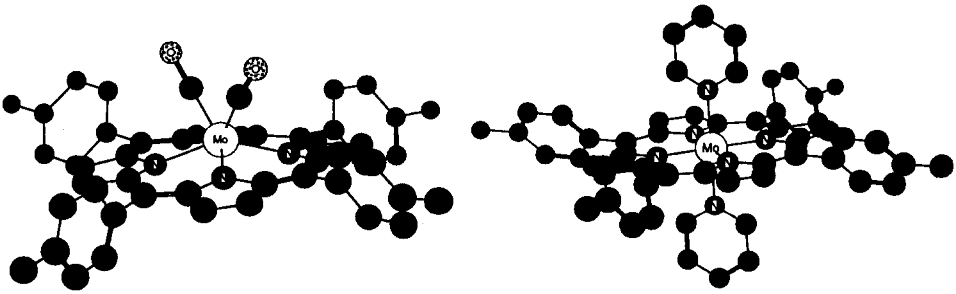


Fig. 8. Crystal structures of $Mo(TpTP)(CO)_2$ (left) and $Mo(TpTP)(Py)_2$ (right) [233].

P≡T*p*TP, OEP, α,γ dimethyletioporphyrin, *meso*-formylOEP, *meso*-aminoOEP, *meso*-isocyanatoOEP, 5-(4-methylphenyl)OEP) have been prepared [223,224,234,235]. Routes into these compounds include the pyrolysis of M(II)(P) precursors such as M(P)(η^2-PhC≡CPh) or M(P)(PEt_3)$_2$ (Eq. (25)). Alternatively, the dimer may be formed directly by reaction of a metal(II) carbonyl with the free base porphyrin (Eq. (26)).

$$2W(OEP)(PEt_3)_2 \xrightarrow{\Delta} [W(OEP)]_2 \tag{25}$$

$$2H_2(OEP) + 2MoCl_2(CO)_4 \xrightarrow{\text{proton sponge}} [Mo(OEP)]_2 \tag{26}$$

The rotation of the metalloporphyrin moieties about the M–M quadruple bond depends only on the strength of the δ-bond. A measurement of this bond strength by variable ^1H NMR arrived at values of about 10–11 kcal mol^{-1} for the Mo derivatives and 12–13 kcal mol^{-1} for W [223,235]. An Mo–Mo bond distance of 2.23 Å for [Mo(OEP)]$_2$ has been estimated from the vibrational frequencies in RR measurements [236], in close agreement with the Mo–Mo bond distance of 2.122(10) Å which was established for [Mo(TPP)]$_2$ by X-ray crystallography [237].

7. Comparison of structural parameters in crystallographically characterized out-of-plane derivatives

It is generally the case that metals with ionic radii between 0.60 and 0.65 Å are easily accommodated in the plane of the N_4 ring. Incorporation of smaller ions causes the entire ring to ruffle to reduce the hole size and, if the metal is only slightly too large, the N_4 core may expand by doming to coordinate the ion. To a first approximation, the ionic radius of a metal as reported by Shannon [117] can be used to anticipate out-of-plane or in-plane coordination geometries; however, as can be seen from the data collected in Table 1, the picture is more complicated and it is clear that other factors must also be taken into consideration in these structural predictions.

For example, all six-coordinate zirconium(IV) derivatives (ionic radius 0.72 Å) studied by X-ray crystallography show cis-coordination of the two ancillary ligands with the central metal displaced 0.9 Å or more out of the N_4 plane. Titanium(IV) compounds (ionic radius 0.605 Å), however, display trans geometries. The ancillary ligands in the M(II) derivatives Ti(T*p*TP)(pic)$_2$ and V(OEP)(THF)$_2$, besides others, are coordinated trans to each other despite the large ionic radii (0.86 Å and 0.79 Å respectively). Since both are paramagnetic high-spin compounds, an important factor for the in-plane coordination might be back bonding from the electron(s) residing in the d_{xz} and (or) d_{yz} orbital(s) into porphyrin orbitals of the same e_g symmetry. Of course with bidentate ligands, as in Ti(T*p*TP)(η^2-S_2) or Ti(OEP)(η^2-PhC≡CPh), the metal is necessarily displaced out of plane.

Another interesting example of the dominance of electronic factors in determining

Table 1
Metric parameters of selected crystallographically characterized metalloporphyrin complexes

M	Porphyrin	Geometry	X	Y	Distance (Å)				Reference
					M=N	$M=N_4$[a]	M=X	M=Y	
Sc[b]	OEP	cis	μ-OH	μ-OH	2.203(2)	0.84	2.076(2)[c]	2.029(1)[c]	[33]
Ti	T*p*TP	trans	4-picoline	4-picoline	2.047(3)	0.0	2.223(3)	2.223(3)	[66]
Ti	TPP	trans	Br	Br	2.062(8)	0.0	2.452(2)	2.454(2)	[54]
Ti	T*p*TP	cis	S[d]	S[d]	2.105(5)	0.658	2.283(2)	2.311(2)	[52]
Zr	OEP	cis	O^tBu	O^tBu	2.293(2)	1.06	1.947(2)	1.948(2)	[78]
Zr	OEP	cis	CH_2SiMe_3	CH_2SiMe_3	2.241(3)	0.93	2.285(4)	2.289(4)	[77]
V	OEP	trans	THF	THF	2.046(4)	0.0	2.174(4)	2.174(4)	[116]
Nb	OEP	cis	O	F	2.211(4)	0.906	1.749(3)	1.888(3)	[127]
Nb	TPP	cis	O	OAc	2.231(6)	1.00	1.720(6)	2.218(4)[e]	[121]
Cr	TPP	trans	py	py	2.018(8)	0.0	2.141(8)	2.141(8)	[141]
Cr	TPP	trans	OPh	THF	2.037(6)	0.0	1.943(10)	2.069(10)	[144]
Mo	TPP	trans	Ph	Cl	2.070(3)	0.089	2.241(4)	2.382(1)	[230]
Mo	T*p*TP	cis	CO	CO	2.14(1)	0.62	1.84(2)	1.87(2)	[233]
Mo	T*p*TP	trans	py	py	2.071(3)	0.0	2.215(3)	2.215(3)	[233]
Mo	T*p*TP	cis	NO	NO	2.165(8)	0.99	1.70(1)[c]	1.70(1)[c]	[231]
Mo	T*p*TP	trans	NO	MeOH	2.091(4)	0.28	1.746(6)	2.284(5)	[231]
W	TPP	cis	O	O_2	2.191[f]	1.49	1.752(13)	1.909(15)[e]	[218]

[a] Displacement of the central metal from the N_4 core. [b] From $[Sc(OEP)(OH)]_2$. [c] Average value. [d] η^2-S_2. [e] Average bond distance between the chelating ligand and the central metal. [f] The porphyrin ring in this molecule is severely distorted resulting in two different sets of M=N bond distances.

the stereochemistry around the central metal is encountered with the d^4 molybdenum compounds *cis*-(MoT*p*TP)(CO)$_2$ vs. *trans*-Mo(T*p*TP)(py)$_2$ and *cis*-Mo(T*p*TP)(NO)$_2$ vs. *trans*-Mo(T*p*TP)(NO)(MeOH). A theoretical treatment addressed the cis vs. trans arrangement in the dicarbonyl and bis-pyridine compound respectively. The preferred geometry in the dicarbonyl was rationalized in terms of stronger interaction of the two carbonyl σ-orbitals with the d_{z^2} and d_{xy} orbitals in the cis isomer than with the d_{z^2} and p_z orbital in the possible trans isomer. In addition, π-bonding also favors the cis isomer. In the high-spin bis-pyridine derivative, single occupation of the d_{z^2} orbital of the Mo(P)-fragment combined with a lack of effective backbonding now slightly favors the trans structure. These crystallographically characterized Mo(II) porphyrin derivatives illustrate an important point: it is not simply the ionic radius alone that influences the geometry about the metal. Rather a fine interplay of steric and electronic factors determines the cis vs. trans coordination geometry. Ligand to metal backbonding might also be responsible for the cis geometry in Mo(T*p*TP)(O)$_2$ vs. a possible trans arrangement. As for other d^0 transition metal dioxo compounds, the trans configuration might be less stable owing to mutual repulsion of two strong σ- and π-donor ligands. However, the photolytic cleavage of one dioxygen moiety might lead to the formation of the kinetic product. A comprehensive review treating cis- and trans-effects in transition metal porphyrins has appeared [238].

8. Relationship of cis-metalloporphyrin structures to metallocenes

Fig. 9 shows a comparison of some of the more important metrical parameters for related compounds. Two main points are apparent from considerations of these data. In general, the Zr–X bond length is marginally shorter in Cp_2Zr derivatives [239] in all cases except the alkoxide where the Zr–O bonds are equivalent within experimental error. Second, for all four porphyrin structures, the X–Zr–X bond angle is considerably more acute (by 11°–17°) than in the d^0 zirconocene analogs. This is no doubt a result of the increased steric demand of the porphyrin as compared with two cyclopentadienyl ligands in these d^0 systems. Similar data have been described for group 4 Schiff base and tetraaza[14]annulene compounds [240–242]. Note, however, that on population of the metallocene a_1 orbital to form related d^1 compounds such as $Cp_2Nb(SPh)_2$ [243] or $[Cp_2MoCl_2]^+$ [239a] the corresponding angles may be much more acute (S–Nb–S 74.8(1)°; Cl–Mo–Cl 82.0(2)°), showing that steric factors *alone* need not necessarily control X–M–X interactions.

9. Conclusions

Recent developments in the field of early transition metal porphyrins have resulted in a considerable expansion in our knowledge of the feasible structural types and have elaborated significantly the range of known reactivities. An important result from the outset of work in this area has been the firm establishment of cis coordina-

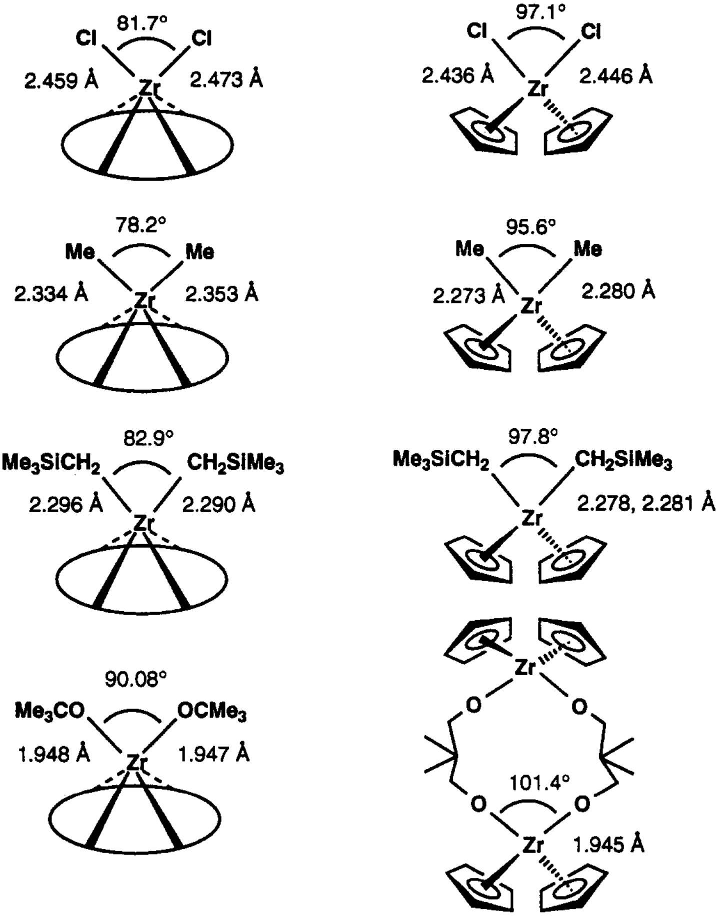


Fig. 9. Comparison of crystal structure data for Zr(OEP) vs. Cp_2Zr derivatives.

tion of additional ligands as a possible geometry. A wide variety of cis ligated metal porphyrins has been prepared, including simple coordination complexes in a range of oxidation states, and highly reactive organometallic derivatives. At this stage of its development, however, the factors influencing coordination geometries at the metal center in early metal porphyrins are not fully understood. For example, in addition to the obvious considerations of the metal ionic radii, it is becoming increasingly apparent that electronic factors may play an important role in determining stereochemistry. In contrast to late transition metal porphyrins, in which reactivity is largely dominated by radical pathways, the presence of cis coordination sites in early transition metal compounds allows reactions such as insertions and oxidations to proceed via non-radical, concerted mechanisms. Therefore, in addition to the analogies drawn with late metal porphyrin systems, it is informative to compare early metal porphyrins with the related metallocene-type systems (i.e. Cp_2MX_{1-3}), especially with regard to their structures and reactivities.

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References

[1] K.M. Smith, Porphyrins and Metalloporphyrins, Elsevier, New York, 1975.
[2] D. Dolphin, The Porphyrins, Vols. 1–4, Academic Press, New York, 1978.
[3] K.M. Kadish, in Advances in Chemistry Series, American Chemical Society, Washington, DC, 1982.
[4] R. Guilard and C. Lecomte, Coord. Chem. Rev., 65 (1985) 87.
[5] D.K. Lavallee, Coord. Chem. Rev., 61 (1985) 55.
[6] P.J. Brothers and J.P. Collman, Acc. Chem. Res., 19 (1986) 209.
[7] R. Guilard, C. Lecomte and K.M. Kadish, Structure Bonding, 64 (1987) 207.
[8] Y. Matsuda and Y. Murakami, Coord. Chem. Rev., 92 (1988) 15.
[9] R. Guilard and K.M. Kadish, Chem. Rev., 88 (1988) 1121.
[10] B. Meunier, Chem. Rev., 92 (1992) 1411.
[11] J.P. Collman, X. Zhang, V.J. Lee, E.S. Uffelman and J.I. Brauman, Science, 261 (1993) 1404.
[12] L.K. Woo, Chem. Rev., 93 (1993) 1125.
[13] C.-P. Wong and W.D. Horrocks, Tetrahedron Lett., (1975) 2637.
[14] P. Richard and R. Guilard, J. Chem. Soc., Chem. Commun., (1983) 1454.
[15] Y. Matsuda, S. Yamada and Y. Murakami, Inorg. Chem., 20 (1981) 2239.
[16] J.W. Buchler, G. Eikelmann, L. Puppe, K. Rohbock, H.H. Schneehage and D. Weck, Liebigs Ann. Chem., 745 (1971) 135.
[17] J.W. Buchler and K. Rohbock, Inorg. Nucl. Chem. Lett., 8 (1972) 1073.
[18] J.W. Buchler and H.H. Schneehage, Tetrahedron Lett., (1972) 3803.
[19] J.W. Buchler, in D. Dolphin (ed.), The Porphyrins, Academic Press, New York, Vol. 1, 1978, p. 389.
[20] C.J. Schaverien, J. Chem. Soc., Chem. Commun., (1991) 458.
[21] C.J. Schaverien and A.G. Orpen, Inorg. Chem., 30 (1991) 4968.
[22] J. Arnold, J. Chem. Soc., Chem. Commun., (1990) 976.
[23] J. Arnold, D.Y. Dawson and C.C. Hoffman, J. Am. Chem. Soc., 115 (1993) 2707.
[24] J.-H. Fuhrhop, K.M. Kadish and D.G. Davis, J. Am. Chem. Soc., 95 (1973) 5140.
[25] J.W. Buchler and H.H. Schneehage, Z. Naturforsch. B, 28 (1973) 433.
[26] G.N. La Mar, G.R. Eaton, R.H. Holm and F.A. Walker, J. Am. Chem. Soc., 95 (1973) 63.
[27] M. Gouterman, L. Karle-Hanson, G.-E. Khalil, J.W. Buchler, K. Rohbock and D. Dolphin, J. Am. Chem. Soc., 97 (1975) 3142.
[28] M. Gouterman, D. Holten and E.L. Lieberman, Chem. Phys., 25 (1977) 139.
[29] W.R. Leenstra, M. Gouterman and A.L. Kwiram, J. Chem. Phys., 71 (1979) 3535.
[30] J.W. Buchler, J. Hüttermann and J. Löffler, Bull. Chem. Soc. Jpn., 61 (1988) 71.
[31] J.W. Buchler and Hammerschmitt, Liebigs Ann. Chem., (1991) 1177.
[32] J. Arnold and C.G. Hoffman, J. Am. Chem. Soc., 112 (1990) 8620.
[33] J. Arnold, C.G. Hoffman, D.Y. Dawson and F.J. Hollander, Organometallics, 12 (1993) 3645.

[34] M.G. Sewchok, R.C. Haushalter and J.S. Merola, Inorg. Chim. Acta, 144 (1988) 47.
[35] M. Tsutsui, R.A. Velapoldi, K. Suzuki and T. Koyano, Angew. Chem., 80 (1968) 914.
[36] J.H. Fuhrhop, Tetrahedron Lett., (1969) 3205.
[37] P. Fournari, R. Guilard, M. Fontesse, J.-M. Latour and J.-C. Marchon, J. Organomet. Chem., 110 (1976) 205.
[38] J.W. Buchler, L. Puppe, K. Rohbock and H.H. Schneehage, Ann. NY Acad. Sci., 206 (1973) 116.
[39] S.S. Eaton and G.R. Eaton, J. Am. Chem. Soc., 97 (1975) 3660.
[40] A.L.W. Shroyer, C. Lorberau, S.S. Eaton and G.R. Eaton, J. Org. Chem., 45 (1980) 4296.
[41] C. Lecomte, J. Protas and R. Guilard, C. R. Acad. Sci., Ser. C, 281 (1975) 921.
[42] R. Guilard, J.-M. Latour, C. Lecomte, J.-C. Marchon, J. Protas and D. Ripoll, Inorg. Chem., 17 (1978) 1228.
[43] J.W. Buchler and L. Puppe, Liebigs Ann. Chem., (1974) 1046.
[44] P.N. Dwyer, L. Puppe, J.W. Buchler and W.R. Scheidt, Inorg. Chem., 14 (1975) 1782.
[45] R. Guilard, M. Fontesse and P. Fournari, J. Chem. Soc., Chem. Commun., (1976) 161.
[46] P. Friant, J. Goulon, J. Fischer, L. Ricard, M. Schappacher, R. Weiss and M. Momenteau, Nouv. J. Chim., 9 (1985) 33.
[47] A. Dedieu, M.-M. Rohmer, H. Veillard and A. Veillard, Nouv. J. Chim., 3 (1979) 653.
[48] T. Malinski, D. Chang, J.-M. Latour, J.-C. Marchon, M. Gross, A. Giraudeau and K.M. Kadish, Inorg. Chem., 23 (1984) 3947.
[49] C.J. Boreham, J.-M. Latour and J.-C. Marchon, Inorg. Chim. Acta, 45 (1980) L69.
[50] M. Inamo, S. Funahashi and M. Tanaka, Inorg. Chim. Acta, 76 (1983) L93.
[51] C. Ratti, P.R.A. Tabard and R. Guilard, J. Chem. Soc., Chem. Commun., (1989) 69.
[52] R. Guilard, C. Ratti, A. Tabard, P. Richard, D. Dubois and K.M. Kadish, Inorg. Chem., 29 (1990) 2532.
[53] M. Nakajima, J.-M. Latour and J.-C. Marchon, J. Chem. Soc., Chem. Commun., (1977) 763.
[54] C. Lecomte, J. Protas, J.-C. Marchon and M. Nakajima, Acta Crystallogr B, 34 (1978) 2856.
[55] J.-C. Marchon, J.-M. Latour, A. Grand, M. Belakhovsky, M. Loos and J. Goulon, Inorg. Chem., 29 (1990) 57.
[56] A.N. Christensen, A. Grand, M.S. Lehmann and D.E. Cox, Acta Chem. Scand., 44 (1990) 103.
[57] E. Forest, J.C. Marchon, J. Ulrich and H. Virelizier, Inorg. Chem., 25 (1986) 3570.
[58] E. Forest, J.C. Marchon, J. Ulrich and H. Virelizier, Org. Mass Spectrom., 22 (1987) 45.
[59] J.-M. Latour, J.-C. Marchon and M. Nakajima, J. Am. Chem. Soc., 101 (1979) 3974.
[60] J.-C. Marchon, J.-M. Latour and C.J. Boreham, J. Mol. Catal., 7 (1980) 227.
[61] C.J. Boreham, G. Buisso, E. Duee, J. Jordanov, J.-M. Latour and J.-C. Marchon, Inorg. Chim. Acta, 70 (1983) 77.
[62] J.-M. Latour, C.J. Boreham and J.-C. Marchon, J. Organomet. Chem., 190 (1980) C61.
[63] A. Deronzier and J.M. Latour, Nouv. J. Chim., 8 (1984) 393.
[64] L.K. Woo, J.A. Hays, R.A. Jacobson and C.L. Day, Organometallics, 10 (1991) 2102.
[65] L.K. Woo and J.A. Hays, Inorg. Chem., 32 (1993) 2228.
[66] L.K. Woo, J.A. Hays, V.G. Young, C.L. Day, C. Caron, F.D'Souza and K.M. Kadish, Inorg. Chem., 32 (1993) 4186.
[67] E.M.K. Mansour, P. Maillard, P. Krausz, S. Gaspard and C. Giannotti, J. Mol. Catal., 41 (1987) 361.
[68] H.J. Ledon and F. Varescon, Inorg. Chem., 23 (1984) 2735.
[69] J.W. Buchler, M. Folz, H. Habets, J. van Kaam and K. Rohbock, Chem. Ber., 109 (1976) 1477.
[70] J.L. Hoard, in K.M. Smith (ed.), Porphyrins and Metalloporphyrins, Elsevier, New York, 1975, p. 347.
[71] J.W. Buchler, A. De Cian, J. Fischer, P. Hammerschmitt and R. Weiss, Chem. Ber., 124 (1991) 1051.
[72] J.W. Buchler, A. De Cian, S. Elschner, J. Fischer, P. Hammerschmitt and R. Weiss, Chem. Ber., 125 (1992) 107.
[73] K. Kim, W.S. Lee, H.-J. Kim, S.-H. Cho, G.S. Girolami, P.A. Gorlin and K.S. Suslick, Inorg. Chem., 30 (1991) 2652.
[74] P.C. Martin, J. Arnold and D.F. Bocian, J. Phys. Chem., 97 (1993) 1332.
[75] O. Bilsel, J.W. Buchler, P. Hammerschmitt, J. Rodriguez and D. Holten, Chem. Phys. Lett., 182 (1991) 415.

[76] B.D. Berezin and T.N. Lomova, Russ. J. Inorg. Chem., 26 (1981) 203.
[77] H. Brand and J. Arnold, J. Am. Chem. Soc., 114 (1992) 2266–2267.
[78] H. Brand and J. Arnold, Organometallics, 12 (1993) 3655.
[79] J. Arnold, S.E. Johnson, C.B. Knobler and M.F. Hawthorne, J. Am. Chem. Soc., 114 (1992) 3996.
[80] H. Brand and J. Arnold, Angew. Chem., Int. Ed. Engl., 33 (1994) 95.
[81] H.-J. Kim, D. Whang, K. Kim and Y. Do, Inorg. Chem., 32 (1993) 360.
[82] S. Ryu, D. Whang, J. Kim, W. Yeo and K. Kim, J. Chem. Soc., Dalton Trans., (1993) 205.
[83] H.-J. Kim, D. Whang, Y. Do and K. Kim, Chem. Lett., (1993) 807.
[84] K. Shibata, T. Aida and S. Inoue, Tetrahedron Lett., 33 (1992) 1077.
[85] K. Shibata, T. Aida and S. Inoue, Chem. Lett., (1992) 1173.
[86] Y.O. Su, R.S. Czernuszewicz, L.A. Miller and T.G. Spiro, J. Am. Chem. Soc., 110 (1988) 4150.
[87] R.S. Czernuszewicz, Y.O. Su, M.K. Stern, K.A. Macor, D. Kim, J.T. Groves and T.G. Spiro, J. Am. Chem. Soc., 110 (1988) 4158.
[88] A. Treibs, Liebigs Ann. Chem., 510 (1934) 42.
[89] A. Treibs, Angew. Chem., 49 (1936) 682.
[90] A. Treibs, Liebigs Ann. Chem., 517 (1935) 172.
[91] K. Ueno and A.E. Martell, J. Phys. Chem., 60 (1956) 934.
[92] M. Tsutsui, R.A. Velapoldi, K. Suzuki, F. Vohwinkel, M. Ichikawa and T. Koyano, J. Am. Chem. Soc., 91 (1969) 6262.
[93] A.D. Adler, F.R. Longo, F. Kampas and J. Kim, J. Inorg. Nucl. Chem., 32 (1970) 2443.
[94] J.W. Buchler and S. Pfeifer, Z. Naturforsch. B, 40 (1985) 1362.
[95] J.G. Erdman, V.G. Ramsey, N.W. Kalenda and W.E. Hanson, J. Am. Chem. Soc., 78 (1956) 5844.
[96] R. Bonnett and P. Brewer, Tetrahedron Lett., (1970) 2579.
[97] R.C. Pettersen and L.E. Alexander, J. Am. Chem. Soc., 90 (1968) 3873.
[98] R.C. Pettersen, Acta Crystallogr B, 25 (1969) 2527.
[99] F.S. Molinaro and J.A. Ibers, Inorg. Chem., 15 (1976) 2278.
[100] H. van Willingen, C.F. Mulks, A. Bouhaouss, M. Ferhat and A.H. Roufosse, J. Am. Chem. Soc., 102 (1980) 4846.
[101] C.F. Mulks and H. van Willigen, J. Phys. Chem., 85 (1981) 1220.
[102] J. Goulon, A. Retournard, P. Friant, C. Goulon-Ginet, C. Berthe, J.-F. Muller, J.-L. Poncet, R. Guilard, J.C. Escalier and B. Neff, J. Chem. Soc., Dalton Trans., (1984) 1095.
[103] R. Hubaut, C.F. Aissi and J. Grimplot, J. Chim. Phys., 88 (1991) 1741.
[104] F.E. Dickson and L. Petrakis, J. Phys. Chem., 74 (1970) 2850.
[105] K.M. Kadish, C. Araullo, G.B. Maiya, D. Sazou, J.-M. Barbe and R. Guilard, Inorg. Chem., 28 (1989) 2528.
[106] V. Thanabal and V. Krishnan, Inorg. Chem., 21 (1982) 3606.
[107] C.M. Newton and D.G. Davis, J. Magn. Res., 20 (1975) 446.
[108] F.A. Walker, E. Hui and J.M. Walker, J. Am. Chem. Soc., 97 (1975) 2390.
[109] M. Lin, M. Lee, K.T. Yue and L.G. Marzilli, Inorg. Chem., 32 (1993) 3217.
[110] F. Vandeneeckoutte, R. Hubault, S. Pietrzyk, T. Des Courieres and J. Grimblot, React. Kinet. Catal. Lett., 45 (1991) 191.
[111] K.A. Macor, R.S. Czernuszewicz and T.G. Spiro, Inorg. Chem., 29 (1990) 1996.
[112] M.G. Drew, P.C.H. Mitchell and C.E. Scott, Inorg. Chim. Acta, 82 (1984) 63.
[113] P. Richard, J.L. Poncet, J.M. Barbe, R.G. Guilard J.A. Rinaldi, A. Cartier and P. Tola, J. Chem. Soc., Dalton Trans., (1982) 1451.
[114] S.M. Pfeifer, Doctoral Dissertation, Technische Hochschule Darmstadt, 1988.
[115] J.-L. Poncet, J.-M. Barbe, R. Guilard, H. Oumous, C. Lecomte and J. Protas, J. Chem. Soc., Chem. Commun., (1982) 1421.
[116] H. Oumous, C. Lecomte, J. Protas, J.L. Poncet, J.M. Barbe and R. Guilard, J. Chem. Soc., Dalton Trans., (1984) 2677.
[117] R.D. Shannon, Acta Crystallogr. A, 32 (1976) 751.
[118] J.-L. Poncet, R. Guilard, P. Friant and J. Goulon, Polyhedron, 2 (1983) 417.
[119] J.L. Poncet, R. Guilard, P. Friant, C. Goulon-Ginet and J. Goulon, Nouv. J. Chim., 8 (1984) 583.
[120] R. Guilard, B. Fliniaux and B.F. Maume, C. R. Acad. Ser. C, 281 (1975) 461.

[121] C. Lecomte, J. Protas, R. Guilard, B. Fliniaux and P. Fournari, J. Chem. Soc., Dalton Trans., (1979) 1306.
[122] M.L.H. Green and J.J.E. Moreau, Inorg. Chim. Acta, 31 (1978) L461.
[123] F. Künzel, Doctoral Dissertation, Technische Hochschule Darmstadt, 1992.
[124] J.F. Johnson and W.R. Scheidt, J. Am. Chem. Soc., 99 (1977) 294.
[125] J.F. Johnson and W.R. Scheidt, Inorg. Chem., 17 (1978) 1280.
[126] C. Lecomte, J. Protas, R. Guilard, B. Fliniaux and P. Fournari, J. Chem. Soc., Chem. Commun., (1976) 434.
[127] C. Lecomte, J. Protas, P. Richard, J.M. Barbe and R. Guilard, J. Chem. Soc., Dalton Trans., (1982) 247.
[128] R. Guilard, P. Richard, M. El Borai and E. Laviron, J. Chem. Soc., Chem. Commun., (1980) 516.
[129] P. Richard and R. Guilard, Nouv. J. Chim., 9 (1985) 119.
[130] Y. Matsuda, S. Yamada, T. Goto and Y. Murakami, Bull. Chem. Soc. Jpn., 54 (1981) 452.
[131] J.E. Anderson, Y.H. Liu, J.M. Barbe and K.M. Kadish, Inorg. Chem., 25 (1986) 3786.
[132] J.E. Anderson, Y.H. Liu, R. Guilard, J.-M. Barbe and K.M. Kadish, Inorg. Chem., 25 (1986) 2250.
[133] Y. Matsuda, S. Sakamoto, H. Koshima and Y. Murakami, J. Am. Chem. Soc., 107 (1985) 6415.
[134] Y. Matsuda, S. Sakamoto, T. Takaki and Y. Murakami, Chem. Lett., (1985) 107.
[135] M. Tsutsui, M. Ichikawa, F. Vohwinkel and K. Suzuki, J. Am. Chem. Soc., 88 (1966) 854.
[136] E.B. Fleischer and T.S. Srivastava, Inorg. Chim. Acta, 5 (1971) 151.
[137] D.A. Summerville, R.D. Jones, B.M. Hoffman and F. Basolo, J. Am. Chem. Soc., 99 (1977) 8195.
[138] N.J. Gogan and Z.U. Siddiqui, Can. J. Chem., 50 (1972) 720.
[139] W.R. Scheidt and C.A. Reed, Inorg. Chem., 17 (1978) 710.
[140] C.A. Reed, J.K. Kouba, C.J. Grimes and S.K. Cheung, Inorg. Chem., 17 (1978) 2666.
[141] W.R. Scheidt, A.C. Brinegar, J.F. Kirner and C.A. Reed, Inorg. Chem., 18 (1979) 3610.
[142] M. Gouterman, L.K. Hanson, G.-E. Khalil, W.R. Leenstra and J.W. Buchler, J. Chem. Phys., 62 (1975) 2343.
[143] G.N. La Mar and F.A. Walker, J. Am. Chem. Soc., 95 (1973) 6950.
[144] A.L. Balch, L. Latos-Grazynski, B.C. Noll, M.M. Olmstead and E.P. Zovinka, Inorg. Chem., 31 (1992) 1148.
[145] K.M. More, G.R. Eaton, S.S. Eaton and K. Hideg, Inorg. Chem., 25 (1986) 3865.
[146] F. Basolo, R.D. Jones and D.A. Summerville, Acta Chem. Scand. A, 32 (1978) 771.
[147] K.R. Ashley, J.G. Leipoldt and V.K. Joshi, Inorg. Chem., 19 (1980) 1608.
[148] P.O. O'Brien and D.A. Sweigart, Inorg. Chem., 21 (1982) 2094.
[149] T. Ozawa and A. Hanaki, Inorg. Chim. Acta, 102 (1985) 169.
[150] S.P. Roe, J.O. Hill and R.J. Magee, Aust. J. Chem., 39 (1986) 1377.
[151] K.S. Suslick and R.A. Watson, New. J. Chem., 16 (1992) 633.
[152] L.A. Bottomley and K.M. Kadish, J. Chem. Soc., Chem. Commun., (1981) 1212.
[153] L.A. Bottomley and K.M. Kadish, Inorg. Chem., 22 (1983) 342.
[154] S.L. Kelly and K.M. Kadish, Inorg. Chem., 23 (1984) 679.
[155] S.A. Klyuev, V.B. Sheinin, B.D. Berezin, D.V. Tsyganov and S.V. Vodzinskii, Bull. Acad. Sci. USSR Div. Chem. Sci., 40 (1992) 1477.
[156] D.M. Guldi, P. Hambright, D. Lexa, P. Neta and J.-M. Savéant, J. Phys. Chem., 96 (1992) 4459.
[157] S.K. Cheung, C.J. Grimes, J. Wong and C.A. Reed, J. Am. Chem. Soc., 98 (1976) 5028.
[158] D.J. Liston, B.J. Kennedy, K.S. Murray and B.O. West, Inorg. Chem., 24 (1985) 1561.
[159] D.J. Liston and B.O. West, Inorg. Chem., 24 (1985) 1568.
[160] J.T. Groves and W.J. Kruper, J. Am. Chem. Soc., 101 (1979) 7613.
[161] L.C. Yuan, T.S. Calderwood and T.C. Bruice, J. Am. Chem. Soc., 107 (1985) 8273.
[162] J.T. Groves and R.C. Haushalter, J. Chem. Soc., Chem. Commun., (1981) 1165.
[163] J.T. Groves, W.J. Kruper, R.C. Haushalter and W.M. Butler, Inorg. Chem., 21 (1982) 1363.
[164] J.W. Buchler, K.L. Lay, L. Castle and V. Ullrich, Inorg. Chem., 21 (1982) 842.
[165] J.R. Budge, B.M.K. Gatehouse, M.C. Nesbit and B.O. West, J. Chem. Soc., Chem. Commun., (1981) 370.
[166] J.T. Groves and W.J. Kruper, Isr. J. Chem., 25 (1985) 148.
[167] S.E. Creager and R.W. Murray, Inorg. Chem., 24 (1985) 3824.

[168] T.G. Traylor and A.R. Miksztal, J. Am. Chem. Soc., 111 (1989) 7443.
[169] J.M. Garrison and T.C. Bruice, J. Am. Chem. Soc., 111 (1989) 191.
[170] J.M. Garrison, R.W. Lee and T.C. Bruice, Inorg. Chem., 29 (1990) 2019.
[171] J. Haber, T. Mlodnicka and J. Poltowicz, J. Mol. Catal., 54 (1989) 451.
[172] G.B. Shul'pin, M.M. Kats and Y.N. Kozlov, Bull. Acad. Sci. USSR Div. Chem. Sci., 37 (1988) 2396.
[173] J. Haber, R. Iwanejko and T. Mlodnicka, J. Mol. Catal., 55 (1989) 268.
[174] R.K. Khanna, J.S. Sutherlin and D. Lindsey, J. Org. Chem., 55 (1990) 6233.
[175] R.K. Khanna, T.M. Pauling and D. Vajpayee, Tetrahedron Lett., 32 (1991) 3759.
[176] L.-C. Yuan and T.C. Bruice, J. Am. Chem. Soc., 107 (1985) 512.
[177] R.L. Elliott, P.J. Nichols and B.O. West, Aust. J. Chem., 39 (1986) 975.
[178] R.L. Elliott and B.O. West, J. Aust. Chem., 41 (1988) 1417.
[179] L.K. Woo, J.G. Goll, L.M. Berreau and R. Weaving, J. Am. Chem. Soc., 114 (1992) 7411.
[180] L.A. Bottomley and F.L. Neely, J. Am. Chem. Soc., 111 (1989) 5955.
[181] J.W. Buchler, C. Dreher, K.-L. Lay, A. Raap and K. Gersonde, Inorg. Chem., 22 (1983) 879.
[182] J.T. Groves, T. Takahashi and W.M. Butler, Inorg. Chem., 22 (1983) 884.
[183] J.W. Buchler and C. Dreher, Z. Naturforsch. B, 39 (1984) 222.
[184] J.H. Penner-Hahn, M. Benfatto, B. Hedman, T. Takahashi, S. Doniach, J.T. Groves and K.O. Hodgson, Inorg. Chem., 25 (1986) 2255.
[185] P.J. Toscano, H. Brand and P.T. DiMauro, Organometallics, 12 (1993) 30.
[186] T.S. Srivastava and E.B. Fleischer, J. Am. Chem. Soc., 92 (1970) 5518.
[187] J.W. Buchler, L. Puppe, K. Rohbock and H.H. Schneehage, Chem. Ber., 106 (1973) 2710.
[188] M.S. Bains and D.G. Davis, Inorg. Chim. Acta, 37 (1979) 53.
[189] Y. Matsuda, F. Kubota and Y. Murakami, Chem. Lett., (1977) 1281.
[190] H.J. Ledon, M.C. Bonnet, Y. Brigandat and F. Varescon, Inorg. Chem., 19 (1980) 3488.
[191] Y. Murakami, Y. Matsuda and S. Yamada, Chem. Lett., (1977) 689.
[192] T. Imamura, M. Terui, Y. Takahashi and T. Numatatsu, Chem. Lett., (1979) 89.
[193] H. Ledon and B. Mentzen, Inorg, Chim. Acta, 31 (1978) L393.
[194] K. Kim, J.W. Sparapandy and J.A. Ibers, Acta Crystallogr. C, 43 (1987) 2078.
[195] T. Imamura and A. Furusaki, Bull. Chem. Soc. Jpn., 63 (1990) 2726.
[196] M. van Dijk, Y. Morita, S. Petrovic, G.M. Sanders, H.C. van der Plas, C.H. Stam and Y. Wang, J. Heterocyclic Chem., 29 (1992) 81.
[197] K. Dehnicke, H. Prinz, W. Kafitz and R. Kujanek, Liebigs Ann. Chem., (1981) 20.
[198] T. Imamura, T. Numatasu, M. Terui and M. Fujimoto, Bull. Chem. Soc. Jpn., 54 (1981) 170.
[199] T. Imamura, M. Takahashi, T. Tanaka, T. Jin, M. Fujimoto, S. Sawamura and M. Katayama, Inorg. Chem., 23 (1984) 3752.
[200] T. Imamura, T. Tanaka and M. Fujimoto, Inorg. Chem., 24 (1985) 1038.
[201] R.G. Hayes and W.R. Scheidt, Inorg. Chem., 17 (1978) 1082.
[202] N. Ohta, W. Scheuermann, K. Nakamoto, Y. Matsuda, S. Yamada and Y. Murakami, Inorg. Chem., 18 (1979) 457.
[203] J. Topich and N. Berger, Inorg. Chim. Acta, 65 (1982) L131.
[204] K.M. Kadish, T. Malinski and H. Ledon, Inorg. Chem., 21 (1982) 2982.
[205] T. Imamura, K. Hasegawa and M. Fujimoto, Chem. Lett., (1983) 705.
[206] K. Hasegawa, T. Imamura and M. Fujimoto, Inorg. Chem., 25 (1986) 2154.
[207] T. Imamura, K. Hasegawa, T. Tanaka, W. Nakajima and M. Fujimoto, Bull. Chem. Soc. Jpn., 57 (1984) 194.
[208] Y. Matsuda, T. Takaki and Y. Murakami, Bull. Chem. Soc. Jpn., 59 (1986) 1839.
[209] G. Legemaat, W. Drenth, M. Schmidt, G. Prescher and G. Goor, J. Mol. Catal., 62 (1990) 119.
[210] P. Hoffmann and B. Meunier, New J. Chem., 16 (1992) 559.
[211] H.J. Ledon, P. Durbut and F. Varescon, J. Am. Chem. Soc., 103 (1981) 3601.
[212] Y. Matsuda, H. Koshima, K. Nakamura and Y. Murakami, Chem. Lett., (1988) 625.
[213] H. Ledon, M. Bonnet and D. Galland, J. Am. Chem. Soc., 103 (1981) 6209.
[214] B. Chevrier, T. Diebold and R. Weiss, Inorg. Chim. Acta, 19 (1976) L57.
[215] K.M. Kadish, D. Chang, T. Malinski and H. Ledon, Inorg. Chem., 22 (1983) 3490.
[216] H. Ledon and M. Bonnet, J. Chem. Soc., Chem. Commun., (1979) 702.

[217] B.F. Mentzen, M.C. Bonnet and H.J. Ledon, Inorg. Chem., 19 (1980) 2061.
[218] C.-H. Yang, S.J. Dzugan and V.L. Goedken, J. Chem. Soc., Chem. Commun., (1985) 1425.
[219] R. Stumpf, Doctoral Dissertation, Technische Hochschule Darmstadt, 1993.
[220] H. Ledon, F. Varescon, T. Malinski and K.M. Kadish, Inorg. Chem., 23 (1984) 261.
[221] H. Ledon and M. Bonnet, J. Mol. Catal., 7 (1980) 309.
[222] T. Malinski, H. Ledon and K.M. Kadish, J. Chem. Soc., Chem. Commun., (1983) 1077.
[223] J.P. Collman and L.K. Woo, Proc. Natl. Acad. Sci., 81 (1984) 2592.
[224] J.P. Collman, J.M. Garner and L.K. Woo, J. Am. Chem. Soc., 111 (1989) 8141.
[225] J. Tachibana and T. Imamura, Chem. Lett., (1990) 2085.
[226] T. Diebold, B. Chevrier and R. Weiss, Angew. Chem., Int. Ed. Engl., 16 (1977) 788.
[227] T. Diebold, B. Chevrier and R. Weiss, Inorg. Chem., 18 (1979) 1193.
[228] J. Colin, B. Chevrier, A. De Cian and R. Weiss, Angew. Chem., Int. Ed. Engl., 22 (1983) 247.
[229] J. Colin, G. Butler and R. Weiss, Inorg. Chem., 19 (1980) 3828.
[230] J. Colin and B. Chevrier, Organometallics, 4 (1985) 1090.
[231] T. Diebold, M. Schappacher, B. Chevrier and R. Weiss, J. Chem. Soc., Chem. Commun., (1979) 693.
[232] A. De Cian, J. Colin, M. Schappacher, L. Ricard and R. Weiss, J. Am. Chem. Soc., 103 (1981) 1850.
[233] J. Colin, A. Strich, M. Schappacher, B. Chevrier, A. Veillard and R. Weiss, New J. Chem., 8 (1984) 55.
[234] J.P. Collman, C.E. Barnes and L.K. Woo, Proc. Natl. Acad. Sci., 80 (1983) 7684.
[235] J.P. Collman, J.M. Garner, R.T. Hembre and Y. Ha, J. Am. Chem. Soc., 114 (1992) 1292.
[236] C.D. Tait, J.M. Garner, J.P. Collman, A.P. Sattelberger and W.H. Woodruff, J. Am. Chem. Soc., 111 (1989) 9072.
[237] C.-H. Yang, S.J. Dzugan and V.L. Goedken, J. Chem. Soc., Chem. Commun, (1986) 1313.
[238] J.W. Buchler, W. Kokisch and P.D. Smith, Structure Bonding, 34 (1978) 79.
[239] (a) K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley and B. Denton, Acta Crystallogr. B, 30 (1974) 2290.
(b) W.E. Hunter, D.C. Hrncir, R.V. Bynum, R.A. Pentilla and J.L. Atwood, Organometallics, 2 (1983) 750.
(c) J. Jeffery, M.F. Lappert, N.T. Luong-Thi, M. Webb, J.L. Atwood and W.E. Hunter, J. Chem. Soc., Dalton Trans., (1981) 1593.
(d) D.W. Stephan, Organometallics, 9 (1990) 1718.
[240] S. De Angelis, E. Solari, E. Gallo, C. Floriani, A. Chiesi-Villa and C. Rizzoli, Inorg. Chem., 31 (1992) 2520.
[241] C. Floriani, S. Ciurli, A. Chiesi-Villa and C. Guastini, Angew. Chem., Int. Ed. Engl., 26 (1987) 70.
[242] F. Corazza, E. Solari, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Chem. Soc., Dalton Trans., (1990) 1335.
[243] M.Y. Darensbourg, R. Silva, J. Reibenspies and C.K. Prout, Organometallics, 8 (1989) 1315.