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A short ride on scorpionates: from d- to f-elements

António Paulo, João D.G. Correia, Maria P.C. Campello, Isabel Santos *

Departamento de Química, Instituto Tecnológico e Nuclear, Estrada Nacional 10, P-2686-953 Sacavém Codex, Portugal

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Abstract

This paper presents an overview of progress involving group 7 elements and actinides with scorpionate ligands. This includes oxides, polyhydrides and carbonyls of group 7 elements and any type of compounds of actinides (III) and (IV). Synthetic procedures, reactivity and structural data are reviewed.

Keywords: Scorpionate ligands; Technetium; Rhenium; Uranium

1. Introduction

All along the periodic table, a rich coordination chemistry has been developed based on the hard scorpionate ligands [1]. Such diversity is due to the easy tunning of the electronic, steric and coordinating properties of scorpionates, achieved by changing the nature of the groups attached to the boron atom (R) and/or by introducing various sterically bulky and/or coordinating groups in the 3- and 5-positions of the pyrazolyl ring (Scheme 1) [1].

Due to their scientific interests, the authors of this manuscript decided to participate in this special issue of Polyhedron with a *short ride on scorpionates*, focused on group 7 elements and actinides. Particular emphasis is given to oxides, polyhydrides and carbonyls of group 7 elements, while for the actinides any type of compound will be reviewed. From group 7, rhenium will be the most extensively described, as oxides, polyhydrides and carbonyls anchored by scorpionates were mainly studied with this element, with a view on stoichiometric or catalytic transformation of substrates [2]. Similar to rhenium, the chemistry of technetium scorpionates is much more limited. This is certainly due to its radioactive nature, although the element is quite relevant to nuclear medicine. Manganese, due to its electronic properties, tends to form mainly homoleptic compounds, which will not be discussed here, but were reviewed elsewhere [1]. Due to accessibility and safety reasons, uranium has been the more extensively studied actinide, and these studies involved mainly U(III) and (IV) compounds anchored by homo- and heteroscorpionates of the first and second generation.

This contribution updates two previous reviews by I. Santos and coworkers [3] one on rhenium poly(pyrazolyl)borates and the other covering both the 4f- and 5f-element chemistry [4]. Special attention will be given to more recent achievements, but to provide some context to the current work, some overlap between this review and its predecessors is unavoidable.

2. Group 7 scorpionate complexes

2.1. M(VII) trioxides

Air-stable M(VII) trioxides [Tp′MO$_3$] (M = Re, Tp′ = Tp (**1a**), pzTp (**1b**), Tp*(**1c**), PhTp (**1d**); M = Tc, Tp′ = Tp (**1a′**), Tp*(**1c′**)) have been prepared by reacting M$_2$O$_7$ (M = Re, Tc) with sodium or potassium salts of the corresponding homoscorpionates [5–9]. Conversion of Re$_2$O$_7$ to ReO$_3$(O$_2$CCF$_3$), followed by reaction with KTp*, is an even more efficient alternative for the synthesis of **1c** (Scheme 2) [10].

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[*] Corresponding author. Tel.: +351-219946066; fax: +351-219941455.

E-mail address: isantos@itn.pt (I. Santos).

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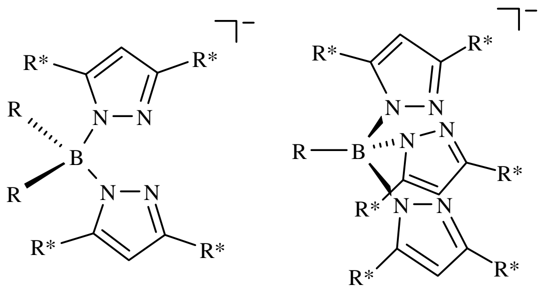


Scheme 1.

Compounds **1a** and **1a′** are also accessible, although in moderate yields, by nitric acid oxidation of [TpMOCl$_2$] (**3a**) (M = Re, Tc) or by reacting [MO$_4$]$^-$ (M = Re, Tc) with excess of NaTp in an acidified alcoholic solution [11,12].

The structures of complexes **1a**, **1b** and **1d** were determined by X-ray diffraction analysis, and found to be almost superimposable. The metal center is six-coordinate by three oxygen atoms and the nitrogens of the tridentate homoscorpionate. The coordination geometry around the metal is pseudo-octahedral and within each compound the Re–N distances (mean values: 2.231(3) Å (**1a**), 2.217(6) Å (**1b**) and 2.222(7) Å (**1d**)) are almost identical. The Re–O bond distances of ca. 1.712(2) Å (**1a**), 1.714(6) Å (**1b**) and 1.710(8) Å (**1d**) are consistent with conventional double bonds [5,7,8]. In the IR spectra of the M(VII) trioxides (M = Re, Tc) the stretching vibrations associated with the M=O bonds appear in the range 890–944 and 853–921 cm^{-1} for the Re and Tc complexes, respectively [5–9]. The solution ^{1}H NMR spectra of **1a–d** are consistent with the respective molecular structure indicating a static behavior for these compounds and precluding, in the case of **1b**, the involvement of the fourth uncoordinated pyrazolyl ring in any scrambling process [7].

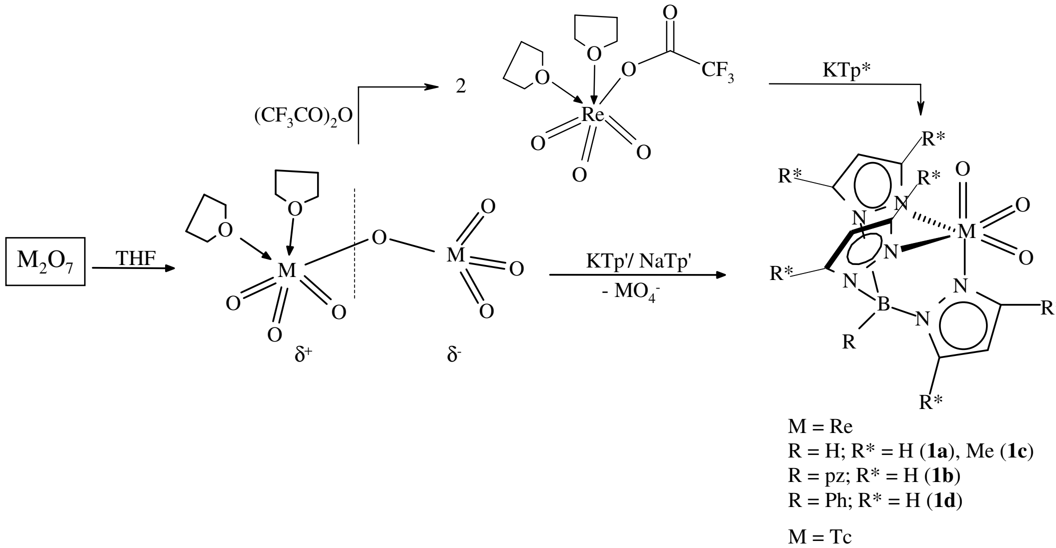
2.2. M(V) oxides

2.2.1. Key compounds

As would be expected for complexes with the metal in the highest oxidation state, the chemistry of the trioxides **1a–d** is dominated by reductive/deoxygenation processes, that led to a certain number of monomeric or dimeric key compounds as entry into Re(V) chemistry, namely [Tp′ReO(μ-O)]$_2$ (Tp′ = Tp (**2a**), pzTp (**2b**)), [Tp′ReOCl$_2$] (Tp′ = Tp (**3a**), pzTp (**3b**), Tp* (**3c**)), [Tp*ReO(OH)Cl] (**4**) and [TpReO(Cl)I] (**5**).

The dimers, [Tp′ReO(μ-O)]$_2$ (Tp′ = Tp (**2a**), pzTp (**2b**)), were obtained by reacting [Tp′ReO$_3$] (Tp′ = Tp (**1a**), pzTp (**1b**)) with PPh$_3$ in THF (Scheme 3) [13,14]. Interestingly, this type of compound was never identified when the scorpionate involved was Tp*. In this case, Gable et al. [15–17] considered the fragment {Tp*ReO$_2$} as being the reduced species, which does not dimerize due to the steric bulkiness of the Tp* ligand.

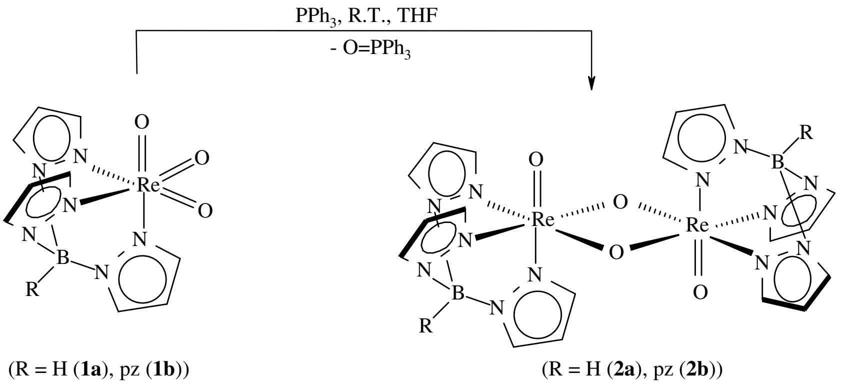
The formulation of **2a**,**b** was mainly based on the spectroscopic properties and reactivity of these compounds. In particular, their IR and mass spectra were consistent with the presence of the [ReO(μ-O)]$_2$ unit [13,14]. Compounds **2a**,**b** are rare examples of scorpionate rhenium complexes exhibiting fluxional behavior in solution. Static ^{1}H NMR spectra could be obtained at low temperature, presenting patterns compatible with the tridentate coordination mode of the scorpionates and with a six-coordination environment around the metal [13,14].



M = Re
R = H; R* = H (**1a**), Me (**1c**)
R = pz; R* = H (**1b**)
R = Ph; R* = H (**1d**)

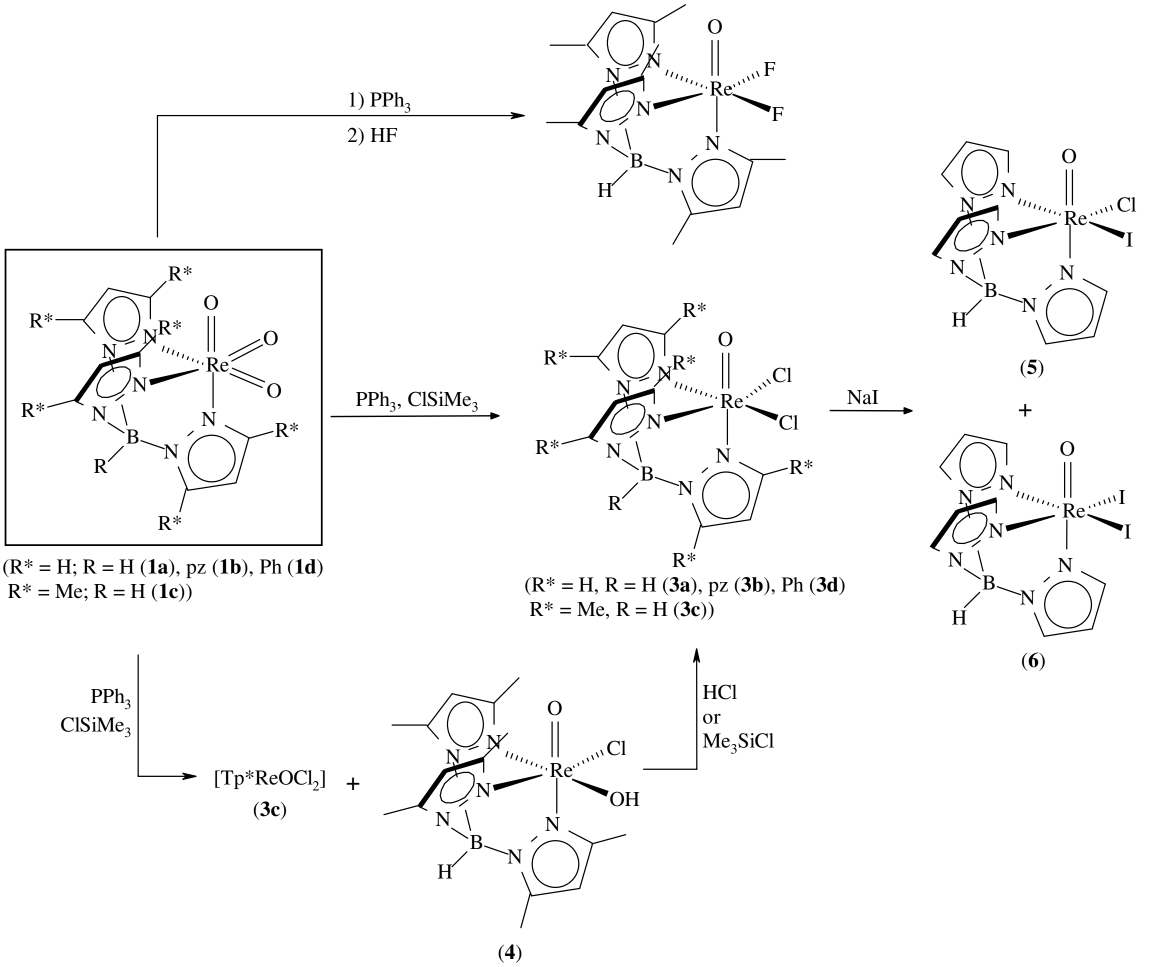
M = Tc
R = H; R* = H (**1a′**), Me (**1c′**)

Scheme 2.



Scheme 3.

As shown in Scheme 4, the oxo-dichlorides [Tp′ReOCl$_2$] (Tp′ = Tp (**3a**), pzTp (**3b**), Tp* (**3c**), PhTp (**3d**)) were synthesized by simultaneous treatment of [Tp′ReO$_3$] (**1a**–**d**) with PPh$_3$ and chlorotrimethylsilane [6–8,10,18,19]. However, during the formation of **3c** hydrolysis also occurs and compound **3c** is obtained contaminated with [Tp*ReO(OH)Cl] (**4**) [6]. Treatment of this mixture with further Me$_3$SiCl or HCl, in a second reaction step, led to the pure oxodichloride **3c** [10,18]. Moreover, optimal conditions for the synthesis of the hydroxychloride [Tp*ReO(OH)Cl] (**4**), a useful precursor for the synthesis of mixed halide Re(V) derivatives, were also described [10]. Compound [Tp*Re(O)F$_2$] was also prepared by reduction of **1c** with PPh$_3$, followed by



Scheme 4.

addition of aqueous HF. In contrast, all the efforts to prepare oxo-difluorides anchored by Tp have failed [20]. The iodide derivatives [TpReO(Cl)(I)] (**5**) and [TpReOI$_2$] (**6**) were prepared by reacting **3a** with sodium iodide (Scheme 4). Replacement of iodide in compound **5** by triflate gave the mixed halide-triflate [TpReO(Cl)(OTf)] [21,23]. Several mixed halides and triflates of the type [Tp*ReO(X)Cl] (X = Br, I, F) and [Tp*ReO(Y)(OTf)] (Y = OH, F, Cl) were also prepared by reacting, respectively, [Tp*ReO(OH)Cl] (**4**) with HX and [Tp*Re(O)Y(F)] with Me$_3$SiOTf [10,20].

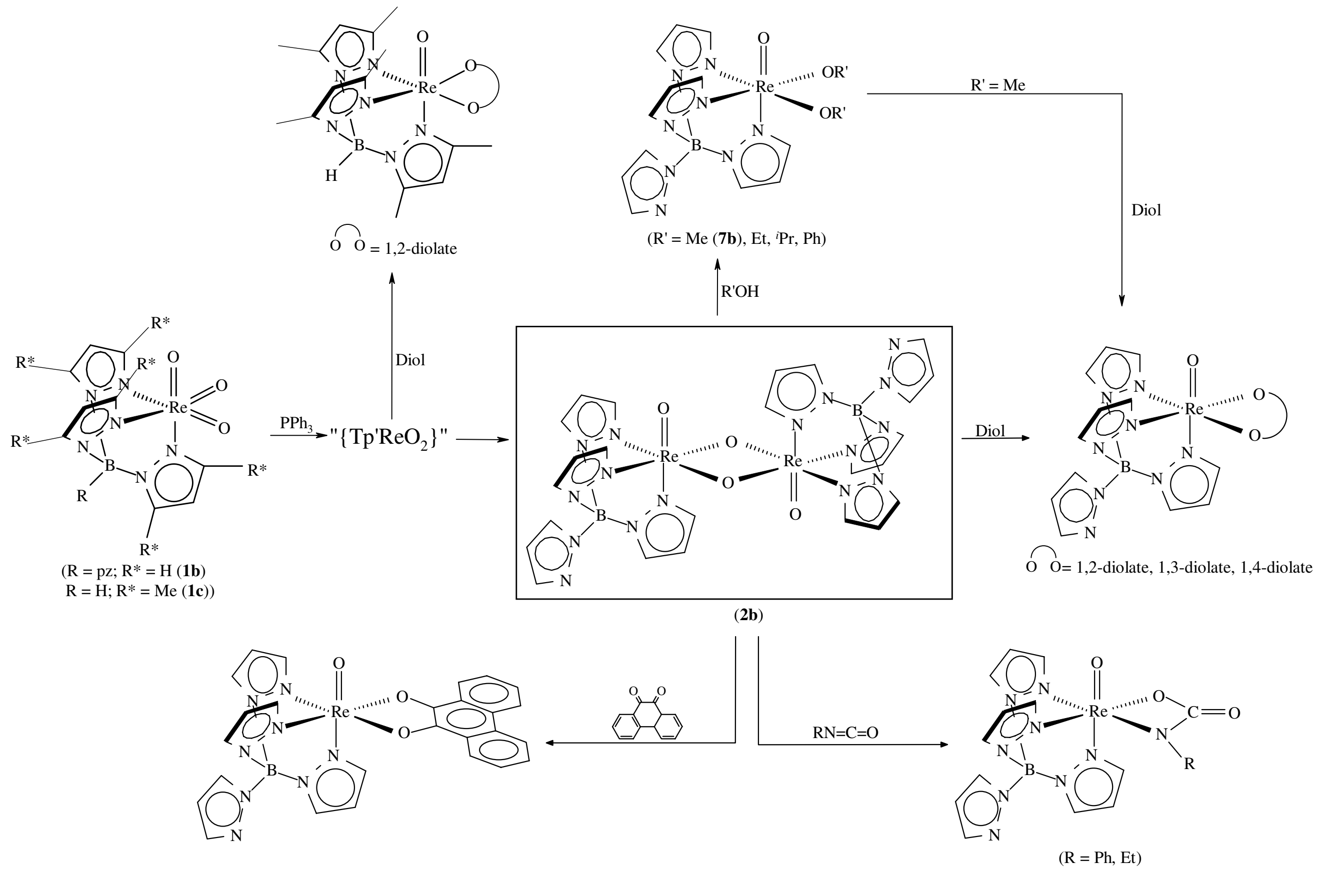
The original synthesis of the key compounds, [TpMOCl$_2$] (M = Re, **3a**, M = Tc, **3a′**), involved reaction of [MO$_4$]$^-$ with excess KTp in aqueous HCl solution and took advantage of the reducing properties of the Tp$^-$ ligand [11,24]. By contrast, the reduction of [ReO$_4$]$^-$ with KTp*, in the presence of HCl, is accompanied by decomposition of the ligand with formation of the dimer [ReOCl$_2$(Hpz^{Me_2})$_2$]$_2$(μ-O) [25]. This symmetric dimer, mixed with the binuclear oxo-bridged asymmetric isomer [{Re(O)Cl(Hpz^{Me_2})$_3$}(μ-O){Re(O)Cl$_3$(Hpz^{Me_2})}] was also identified in the reaction of KTp* with [N^{n}Bu$_4$][ReOCl$_4$] [18]. When the metal is Tc, the precursor [N^{n}Bu$_4$][TcOX$_4$] (X = Br, Cl) reacts with excess Tp yielding [TpTcOX$_2$] as the main product [26]. The isoelectronic sulfido complexes [TpMSCl$_2$] (M = Re, Tc) have been directly prepared from **3a** and **3a′** by atom transfer from B$_2$S$_3$, without degradation of the ancillary scorpionate [27–29].

2.2.2. Derivative chemistry of M(V) scorpionate oxides

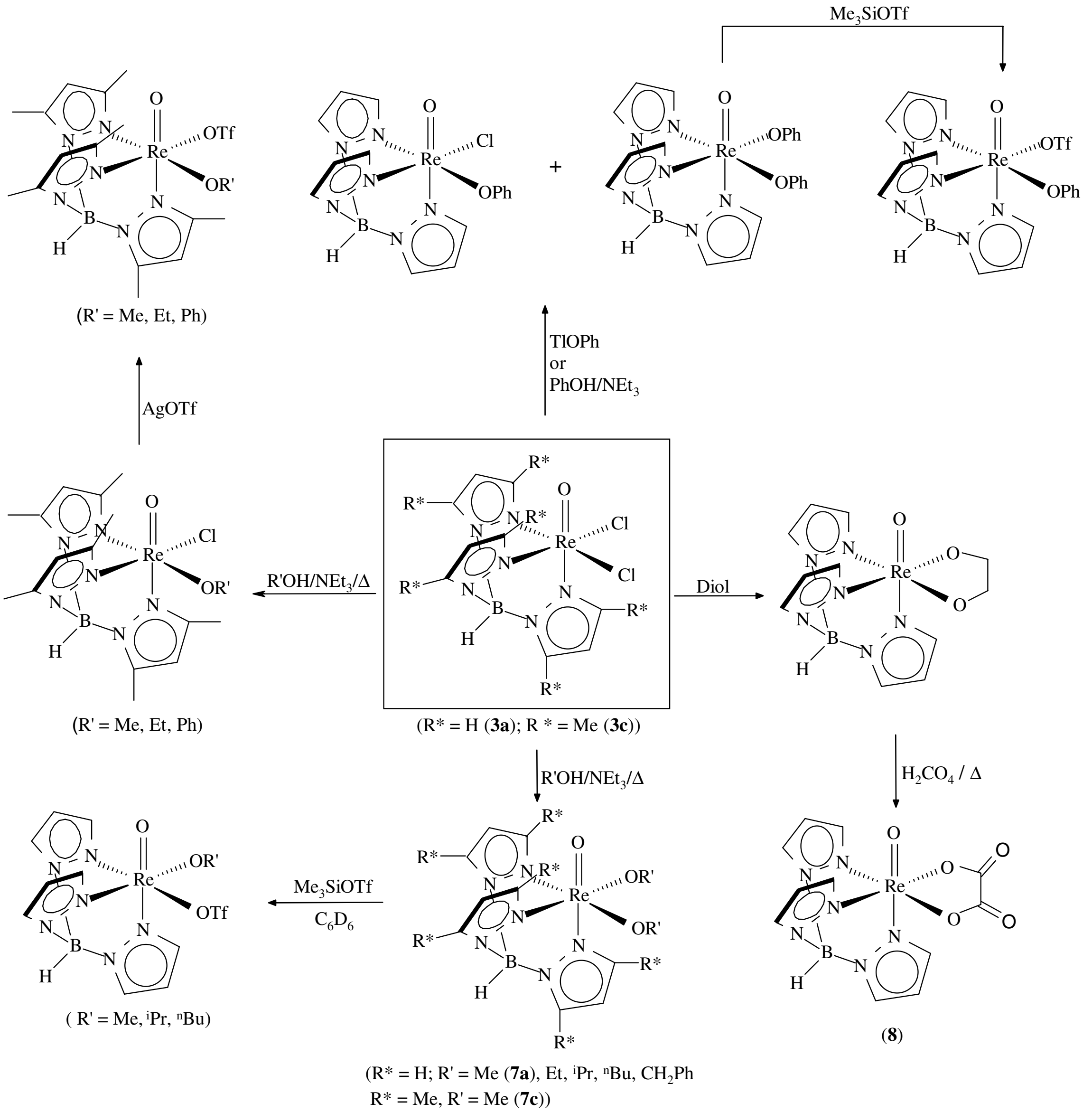
2.2.2.1. Complexes with oxygen donor co-ligands. Several oxocomplexes with alkoxides, diolates or other oxygen donor co-ligands have been isolated using the dinuclear compounds [Tp′ReO(μ-O)]$_2$ (Tp′ = Tp(**2a**), pzTp (**2b**)) or the in situ generated {Tp*ReO$_2$} fragment as starting materials [13–15]. The reaction of the bis-metoxide [(pzTp)ReO(OMe)$_2$] (**7b**) with diols is also a quite convenient approach for the synthesis of diolates (Scheme 5) [30].

Preparation of this type of compounds was also achieved using the monomeric dichlorides [Tp′ReOCl$_2$] (Tp′ = Tp (**3a**), Tp* (**3c**)) as precursors (Scheme 6) [10,31]. However, comparatively to the synthetic procedures depicted in Scheme 5, this synthetic route is time consuming, demands high temperatures and the use of deprotonating agents.

While the alkoxide derivatives [Tp′ReO(OR′)$_2$] (Tp′ = Tp, pzTp) are somewhat air and moisture sensitive, decomposing mainly to the dimers [Tp′ReO(μ-O)]$_2$ (Tp′ = Tp (**2a**), pzTp (**2b**)), the bisalkoxides anchored by



Scheme 5.



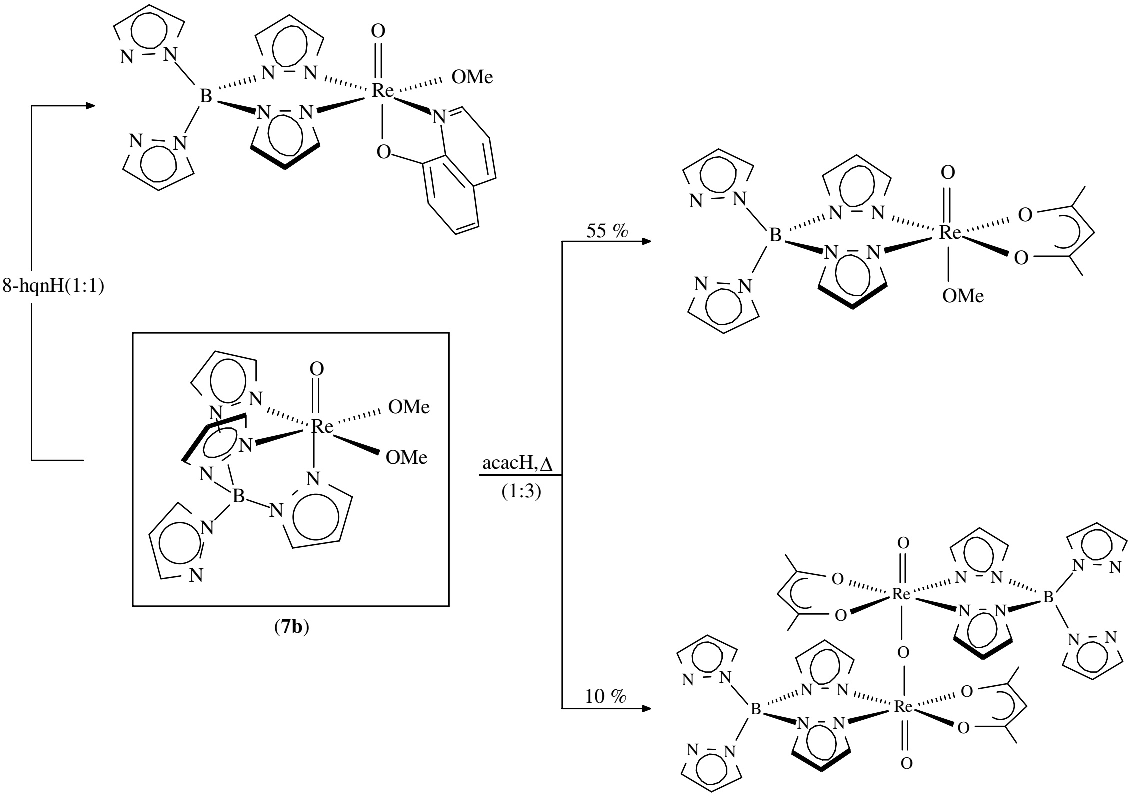
Scheme 6.

Tp* are stable in solution, even after several days [10,13,31]. Vicinal diolates of the type [Tp′ReO(O∩O)] (Tp′ = Tp, pzTp, Tp*) are air and water resistant but their thermolysis regenerates [Tp′ReO$_3$] (Tp′ = Tp (**1a**), pzTp (**1b**), Tp* (**1c**)) and the corresponding alkene [12,15,30,33]. In contrast, the complexes [(pzTp)ReO{O(CH$_2$)$_n$O}] ($n = 3, 4$) hardly eliminate the corresponding olefin under the same conditions [30]. The oxalate [TpReO(C$_2$O$_4$)] (**8**) is also thermally robust [33].

Characterization of this family of compounds, in some cases, also included X-ray structural analysis: [(pzTp)ReO(OPh)$_2$], [(pzTp)ReO(OMe)$_2$] (**7b**), [TpReO(OTf)$_2$], [TpReO(C$_2$O$_4$)] (**8**) and [(pzTp)ReO{O(CH$_2$)$_2$O}]. All are monomeric and the metal is six-coordinate, displaying a distorted octahedral coordination geometry. The homoscorpionate occupies one triangular face of the coordination polyhedron and the oxygen atoms of the two alkoxides or diolate are in the equatorial plane [13,30,32–34].

The nucleophilicity of the Re=O functionality in some of these alkoxide and diolate derivatives allowed the synthesis of the stable Lewis acid–metal complex adducts [TpRe{OB(C$_6$F$_5$)$_3$}(OEt)$_2$], [TpRe{OB(C$_6$F$_5$)$_3$}(OCH$_2$CH$_2$O)], and [TpRe{OB(C$_6$F$_5$)$_3$}(C$_2$O$_4$)], which were prepared by reacting the corresponding monoxocompounds with the strong Lewis acid B(C$_6$F$_5$)$_3$ [35].

Corroborating the versatility of the pzTp systems, reactions of [(pzTp)ReO(OMe)$_2$] (**7b**) with protic oxygen donor substrates, potentially bidentate and uninegative, promoted a haptotropic change of the anchor scorpionate from κ^3-pzTp to κ^2-pzTp (Scheme 7) [36].



Scheme 7.

The bidentate coordination of pzTp in [(κ^2-pzTp)ReO(acac)(OMe)] and [(κ^2-pzTp)ReO(acac)]$_2$(μ-O) was confirmed by X-ray crystallography. In these six-coordinate octahedral complexes, the oxo groups occupy the axial sites and the κ^2-pzTp and acac ligands lie in the equatorial plane. The dimeric structure of [(κ^2-pzTp)ReO(acac)]$_2$(μ-O) is centrossymmetric, with a quasi linear O=Re–O–Re=O group. The bridging Re–O bond length, 1.910(1) Å, is normal for rhenium complexes containing this type of moiety [36].

2.2.2.2. Complexes with nitrogen-donor co-ligands. Re(V) oxo amido derivatives of the type [TpReOCl(NRR′)] have been isolated by reacting [TpReOCl$_2$] (**3a**) with excess of the corresponding amines (Scheme 8). These oxo-amidos are unstable in solution, decomposing in the presence of air to [TpReO$_3$] (**1a**), and exist in solution as conformational isomers, most likely due to restricted rotation about the Re–N bond [37].

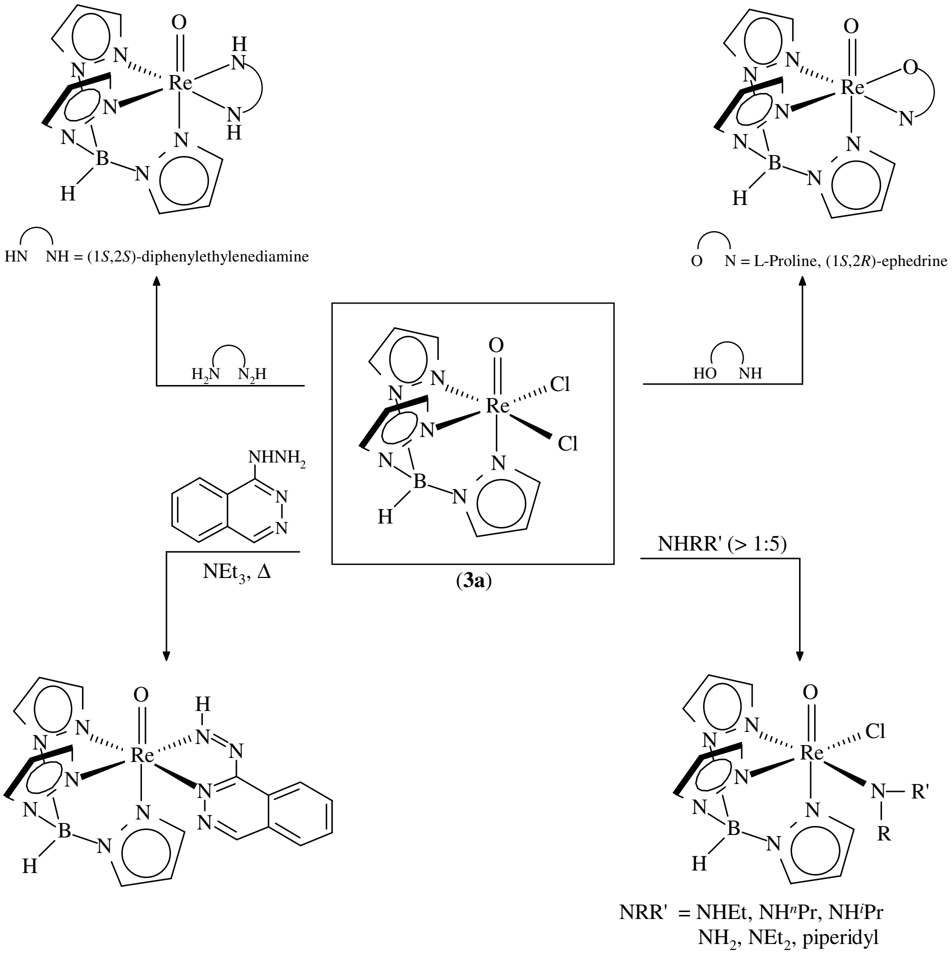
Compound **3a** was also used as precursor in the synthesis of metallacycles of the type [TpReO(κ^2-N–X)] (X = N, O) [38,39]. Some of these compounds contain chiral and bidentate ligands of the type alcoholate or amidate, derived from (1*S*,2*R*)-ephedrine, (1*S*,2*S*)-diphenylethylenediamine, and L-proline (Scheme 8) [38].

Monomeric and dimeric derivatives containing metal–nitrogen bonds were prepared by reacting [(pzTp)ReO(μ-O)]$_2$ (**2b**) or [(pzTp)ReO(OMe)$_2$] (**7b**) with diamines or pyrazoles (Scheme 9) [36]. Diamines react with **2b** or **7b** yielding the monomeric metallacycles [(pzTp)ReO($HN^{\cap}NH$)], while reactions of **2b** with pyrazoles afforded dimeric species with bridging pyrazolides. **7b** also reacts with pyrazoles and forms the monomeric **9a**,**b**, which slowly dimerize in solution to **10a**,**b**, releasing pyrazole and methanol (Scheme 9) [36].

The crystal structure of **10a** consists of two independent "{κ^2-(pzTp)ReO}" units triple bridged by an oxygen and two pyrazolide ligands. The O=Re–O–Re=O unit is quite bent (Re–O–Re, 125.4(3)°) due to the steric requirements of the two bridging pyrazolides [36]. This quite unusual structure was also found in the recently described [{κ^2-H(F)Bpz$_2$}Re(O)]$_2$(μ-pz)$_2$(μ-O), obtained by refluxing [TpReOI$_2$] with excess of NaF in acetonitrile [20].

Re(V) imido compounds of general formula [TpRe(NTol)X$_2$] were synthesized by reacting [TpReOX$_2$] (X = Cl (**3a**), I (**6**)) with *p*-toluidine (Scheme 10) [37,40]. Based on [TpRe(NTol)X$_2$] (X = Cl, I) several Re(V) imido alkyl and aryl derivatives have been prepared by methatesis reactions (Scheme 10) [40].

The imido group being isoelectronic with the oxo ligand produces similar types of complexes, as far as general structural patterns are concerned. However, from the electronic point of view the imido derivatives



Scheme 8.

are more electron-rich compounds. This trend was confirmed by electrochemical studies performed on a series of imido and oxo-complexes of the type [TpRe(NTol)(X)(Y)] and [TpReO(X)(Y)] (X, Y = triflate, halide, alkyl, aryl). Consistently, the oxo-complexes act as inner-sphere oxidants, reacting as electrophiles towards PPh_3, in contrast with the imido congeners [41].

2.2.2.3. Complexes with sulfur donor-co-ligands. Mono- or bis-thiolates and dithiolates have been synthesized by reacting [$TpReOCl_2$] (**3a**) and the corresponding mono- or bidentate thiols in the presence of deprotonating agents and/or under reflux (Scheme 11) [19,28,39]. Thiophenolates [Tp*ReO(OH)(SPh′)] were also obtained by treatment of [Tp*ReO(Cl)(OH)] (**4**) with the corresponding thiol [6].

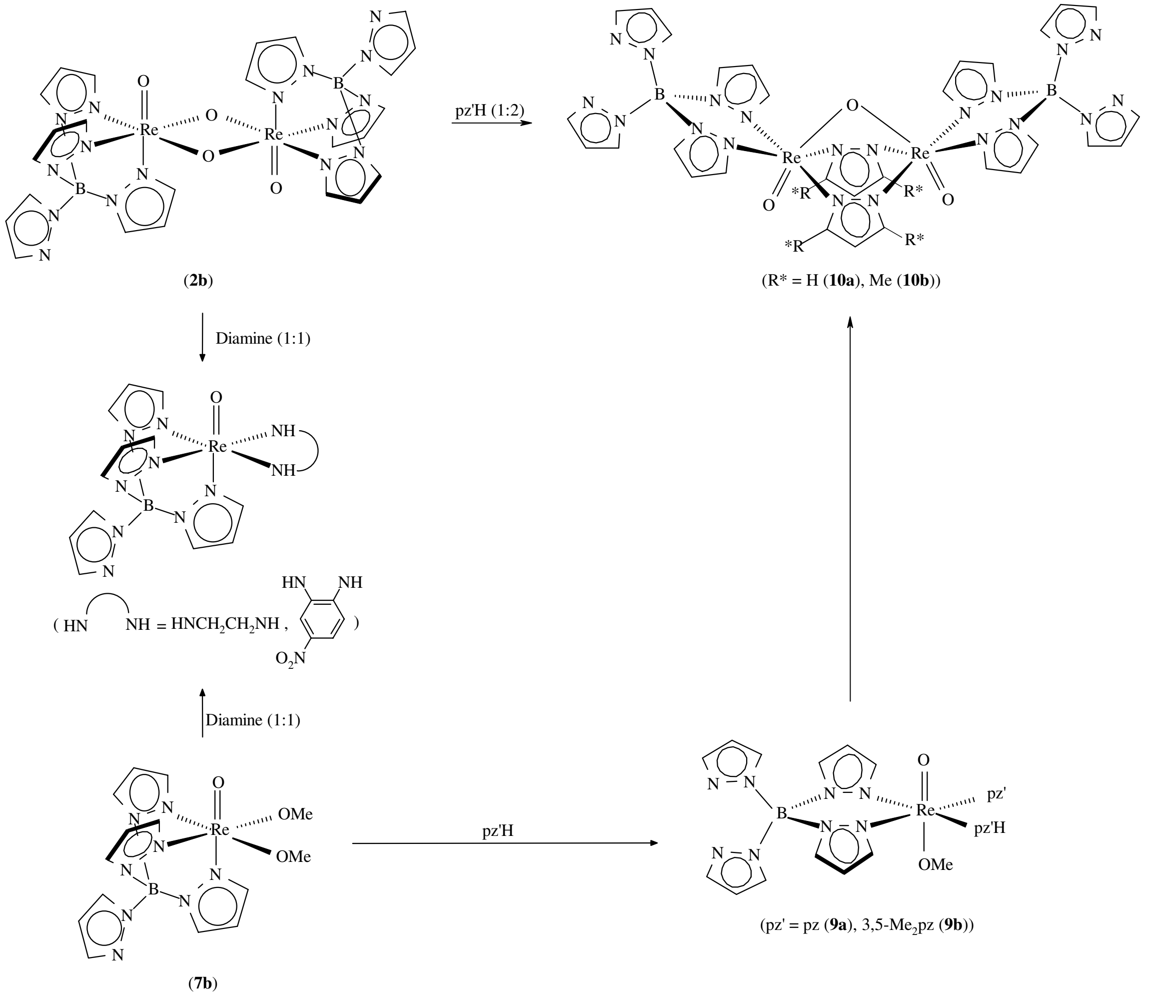
A faster and cleaner procedure for the preparation of thiolate derivatives is the reaction of the dinuclear compound [(pzTp)ReO(μ-O)]$_2$ (**2b**), or the in situ generated {Tp*ReO_2} unit, with thiols, 2-mercaptopyridine, 2-mercaptoalcohols or dithiol (Scheme 12) [13,17,42,43].

The compounds [TpReOCl(SPh)], [TpReO(SCH_2CH_2S)], [Tp′ReO$(SPh)_2$] and [Tp′ReO(2-S-py)$_2$] (Tp′ = Tp, pzTp) were structurally characterized. All are six-coordinate by a κ^3-Tp′, an oxo group and two monodentate or one bidentate co-ligand, displaying an octahedral coordination geometry [13,19,28,39,43].

An interesting result, which confirmed the haptotropism of pzTp, was the identification of the complex [(κ^2-pzTp)ReO{κ^2-(C_5H_4NS)}(OMe)], obtained by reacting [(pzTp)ReO$(OMe)_2$] (**7b**) with 2-mercaptopyridine. As shown by the solid state structural analysis, the metal is six-coordinate by the κ^2-pzTp, the κ^2-pyS and by a metoxide group coordinate *trans* to the oxo (Scheme 12) [43].

2.2.2.4. Complexes with hydrocarbyl co-ligands. Oxo alkyl or aryl derivatives were prepared by reacting [Tp′$ReOCl_2$] (Tp′ = Tp (**3a**), Tp* (**3c**)) with different alkylating agents (Scheme 13) [10,32,44].

The outcome and yield of these reactions depend on the nature of the scorpionate and also on the alkylating agent. It was found that the Tp* system was more resistant to reduction, making possible the use of



Scheme 9.

Grignard reagents in the arylation. Mayer and co-workers [10] considered that steric factors, more than electronic ones, are responsable for the greater stability of the Tp* organometallic derivatives. Substitution of the halide in [Tp′ReO(X)(R′)] (Tp′ = Tp; X = Cl, R′ = Me, Et, ^{n}Bu, Ph; X = I, R′ = Ph and Tp′ = Tp*, X = Cl, R′ = Et, Ph) by reaction with silver triflate led to [Tp′ReO(OTf)(R′)] [10,32,44]. Unlike the reactions with complexes containing the Tp* ligand, in the case of Tp complexes the reactions require some days for completion, but excess of AgOTf cannot be used due to separation problems.

Some of these organometallic Re(V) oxides were characterized by single crystal X-ray diffraction analysis. The complexes adopt a distorted octahedral geometry with the rhenium atom displaced toward the oxo ligand, similar to other oxo Re(V) scorpionate compounds containing different co-ligands [10,44].

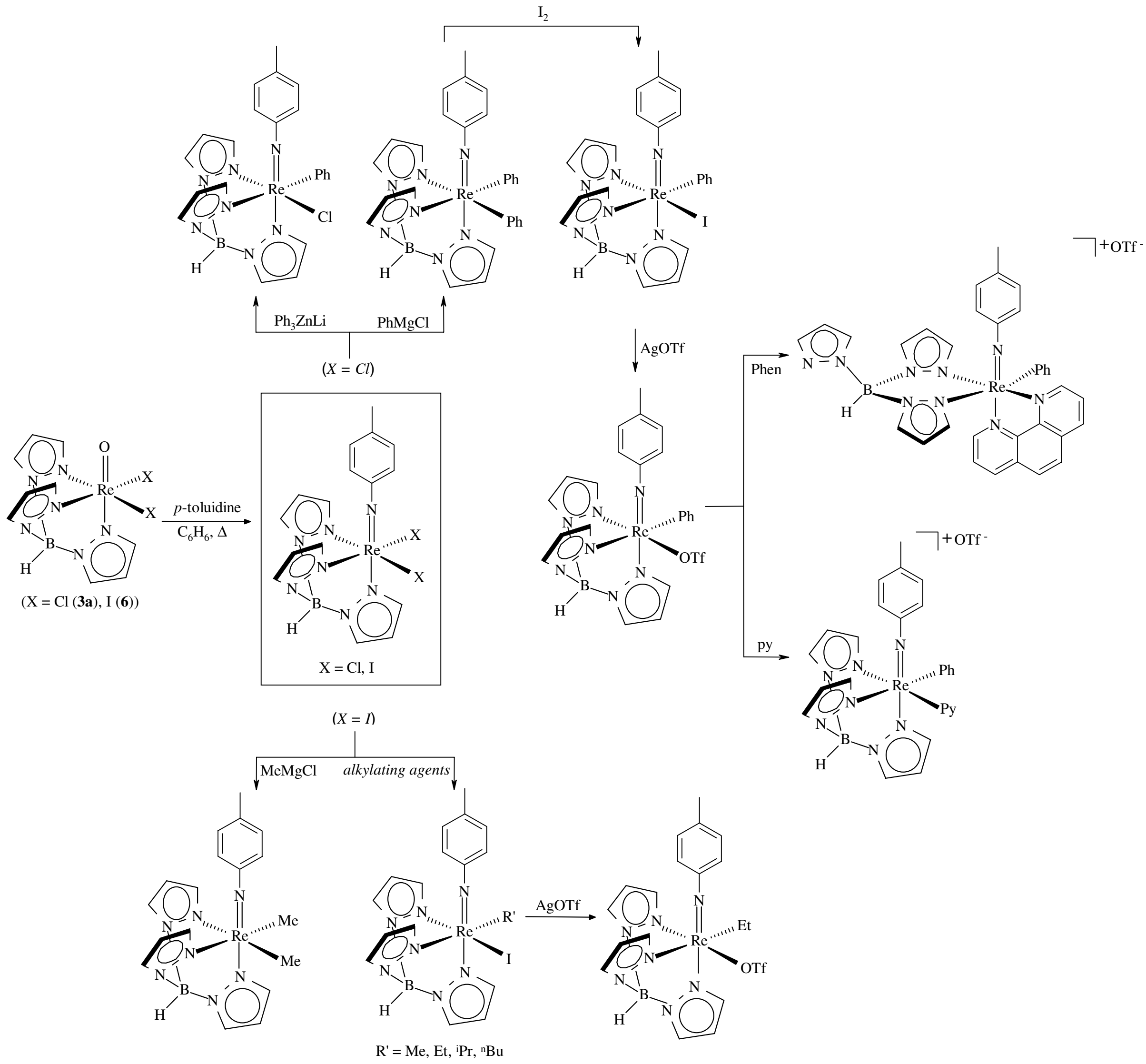
2.2.3. *trans-Dioxocomplexes*

trans-Dioxo derivatives, of general formula *trans*-[(κ^2-Tp′)ReO$_2$L$_2$] (**11**–**16**), were obtained by reducing [Tp′ReO$_3$] (Tp′ = Tp (**1a**), pzTp (**1b**), PhTp (**1d**)) with PPh$_3$ in the presence of σ donors such as pyridines, imidazoles or diphosphines (L) (Scheme 14) [8,45,46]. The stability of this unusual class of compounds depends on the scorpionate and on the neutral co-ligand. Santos et al. found a higher stability for the pzTp system and identified the dimers [Tp′ReO(μ-O)]$_2$ (**2**) as the major decomposition products.

The synthesis of **11**–**16** was considered to be consistent with the formation of the electronic and coordinatively unsaturated "{Tp′ReO$_2$}" fragment, which does not dimerize in the presence of neutral σ donor ligands but yields **11**–**16**. The $\kappa^3 \Longleftrightarrow \kappa^2$-haptotropism of the scorpionates facilitates the process [8,45,46].

The structural analysis of some *trans*-dioxocomplexes (**11c**, **13**, **15a**, **15b**) confirmed the κ^2-coordination mode of the scorpionate ligands and the presence of the *trans*-ReO$_2$ unit. The Re–O bond distances (1.751–1.773) are typical of Re(V) *trans*-dioxocomplexes and are compatible with a certain double character [45,46].

During recrystallization of **15a** a slight decomposition occurred and a pzH molecule of solvation per



Scheme 10.

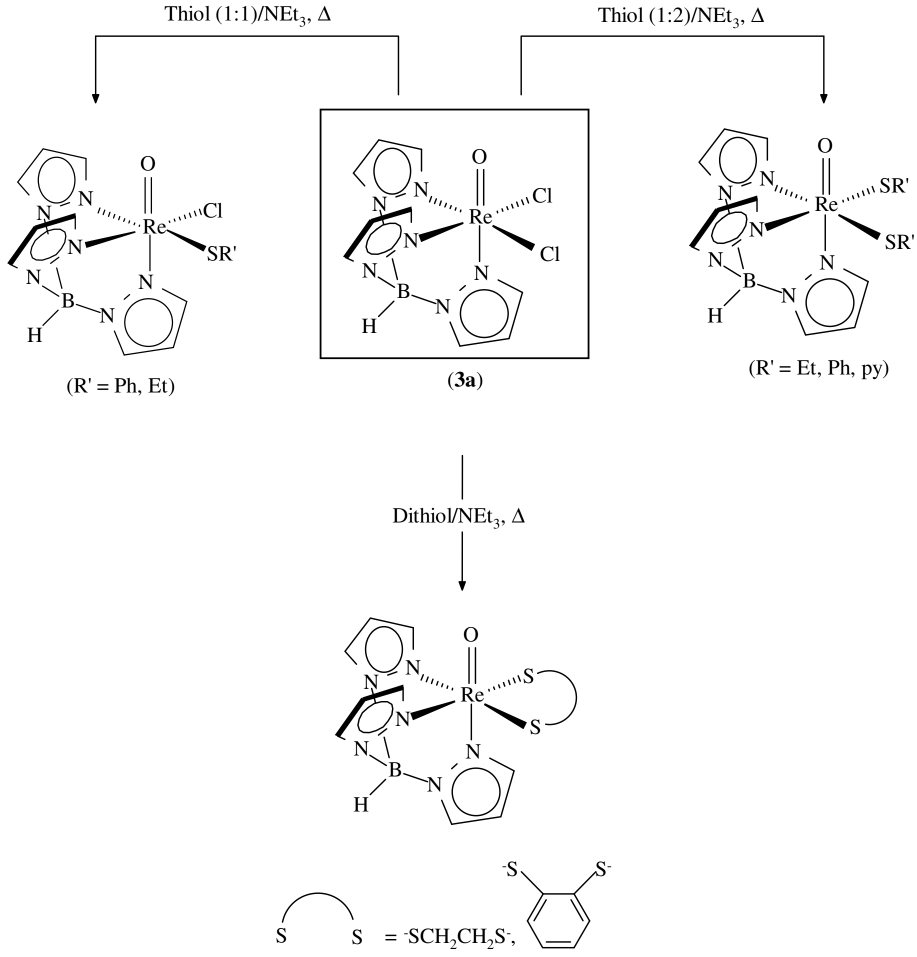
asymmetric unit appears in the crystal structure. Another indication for the relative instability of **15a** is the formation of *trans*-$[ReO_2(dmpe)_2]$ [Tp] (**17**), due to the replacement of Tp by dmpe moiety. The crystal structure of **17** consists of *trans*-$[ReO_2(dmpe)_2]^+$ cations and Tp anions, representing a rare example of a d-transition complex with a scorpionate acting as counter-ion [46].

The ^1H NMR spectra of the dioxocomplexes anchored by κ^2-pzTp show abnormally highfield shifted H(3/5) resonances for the two uncoordinated pyrazolyl rings. This behavior is typical of Re(V) oxocomplexes with κ^2-pzTp ligand, and rendered ^1H NMR spectroscopy a powerful tool in assigning the denticity of the pzTp ligand [36,45].

When the synthesis of *trans*-$[(\kappa^2\text{-pzTp})ReO_2(py)_2]$ was tried using *trans*-$[ReO_2(py)_4]Cl$ as starting material, an oxygen attack at the boron atom was observed and a mixture of two compounds anchored by asymmetric κ^2-heteroscorpionates was obtained (Scheme 15) [45].

Reactions of the starting material *trans*-$[ReO_2(py)_4]$ Cl with Bp or Bp* were also studied. No degradation of the scorpionates was observed and the resulting compounds were the anions *trans*-$[(Bp')_2ReO_2]^-$ (Bp′ = Bp, Bp*), with *trans*-$[ReO_2(py)_4]^+$ as counter ion (Scheme 15). These anionic complexes react readily with the electrophilic substrates $ClXMe_3$ (X = Si, Sn), affording $[(Bp')_2ReO(OXMe_3)]$ and providing an easy entry into the chemistry of bis-Bp′ oxocompounds (Scheme 15) [47].

Unusual cationic mono-oxocomplexes of general formula $[(\kappa^2\text{-pzTp})ReO(OSiMe_3)(L)_2]Cl$ were also synthesized by reacting *trans*-$[(\kappa^2\text{-pzTp})ReO_2(L)_2]$ with trimethylsilyl chloride (Scheme 16). In solution, the cationic complexes with monodentate σ-donor ligands



Scheme 11.

rearrange to the neutral compounds [(κ^2-pzTp)ReO(OSiMe$_3$)Cl(L)]. The use of dmpe improved considerably the stability of the cationic species, preventing such rearrangement (Scheme 16) [48].

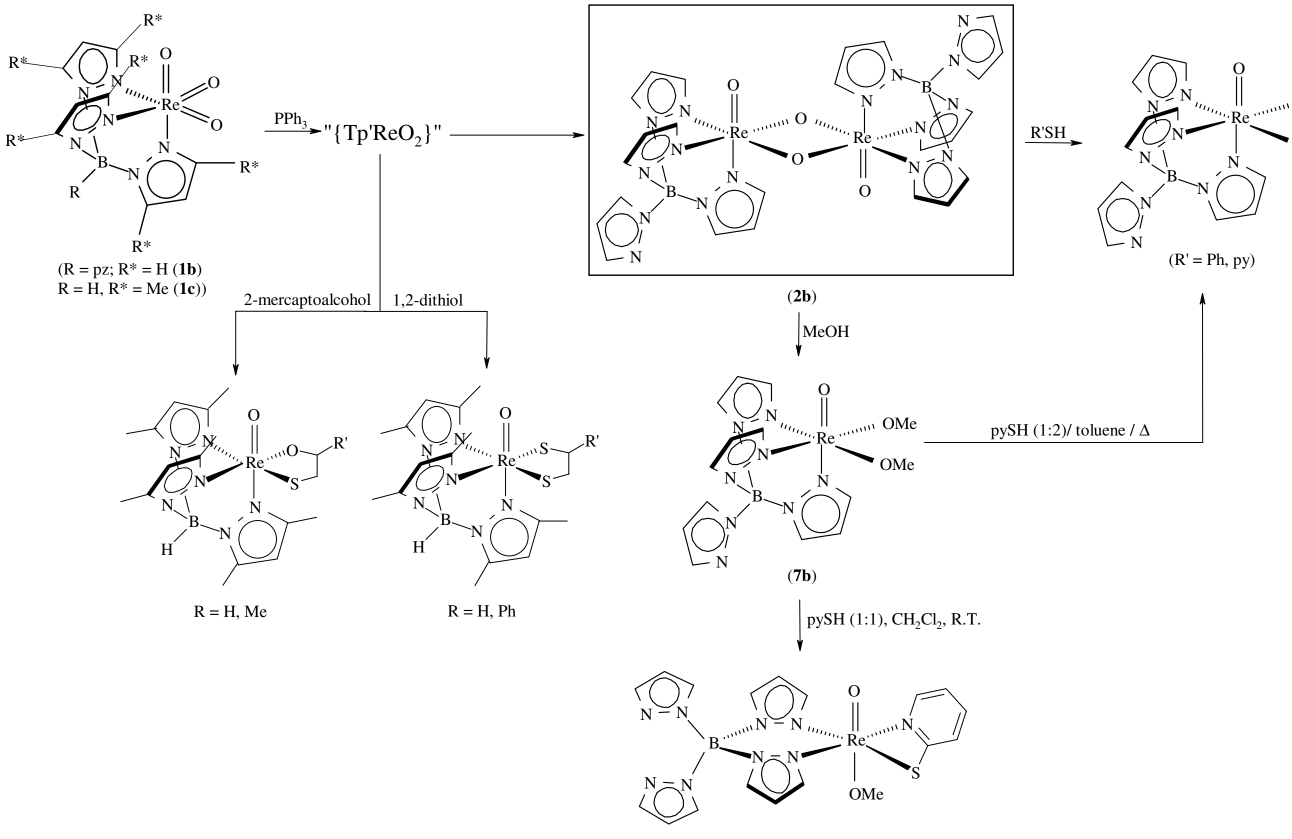
2.2.4. Oxygen transfer reactions

Re(III) monomeric adducts of the type [Tp′ReX$_2$L] (Tp′ = Tp, X = Cl, L = PPh$_3$, py, 3-hexyne, OPMe$_3$; X = Br, L = py, Meim, OPEt$_3$; Tp′ = pzTp, X = Cl, L = PPh$_3$, PEtPh$_2$, PEt$_2$Ph, PEt$_3$) or the pyridine adducts [TpReCl(X)py] (X = OPh, NEt$_2$) were obtained by deoxygenation of [Tp′ReOX$_2$] or [TpReOCl(X)] (X = OPh, NEt$_2$) with tertiary phosphines or phosphites, respectively (Scheme 17) [34,37,49,50].

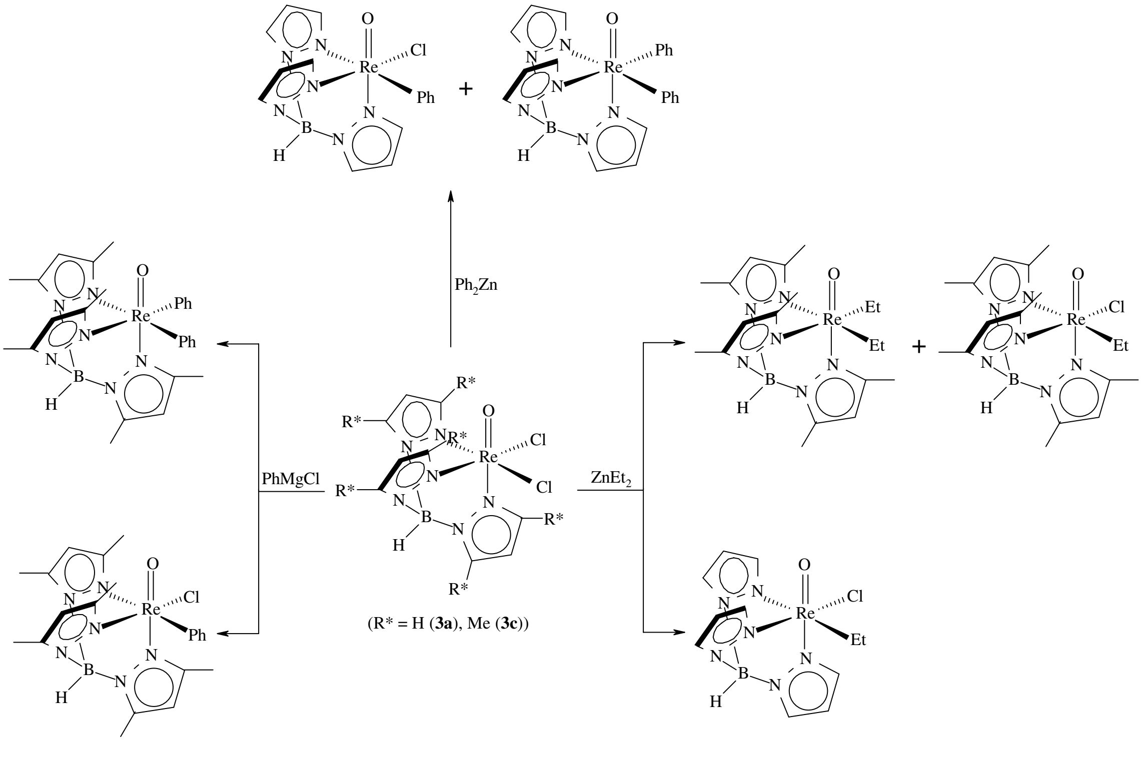
When oxygen abstraction in [TpReOCl$_2$] (**3a)** is carried out with PMe$_3$, in the presence of 2,2-bipyridine and thallium triflate, the complex formed is cationic and has been formulated as [TpRe(κ^2-bipy)(Cl)][OTf]. Further reduction of this cationic compound with Zn/Hg in the absence or presence of cyclopentene yields [TpRe(κ^2-bipy)(Cl)] and [TpRe(κ^2-bipy)(η^2-cyclopentene)], respectively [51]. The paramagnetic [(pzTp)ReCl$_3$] has also been identified in the reaction of [ReOCl$_3$(PPh$_3$)$_2$] with K(pzTp) in CH$_2$Cl$_2$. This compound was considered to be formed through a Re(III) intermediate species, which is unstable and easily oxidized by the solvent (Scheme 18) [30].

The octahedral Re(III) complexes, anchored by Tp or pzTp, and [(pzTp)ReCl$_3$] are all paramagnetic and present relatively sharp but shifted resonances in the ^{1}H NMR spectra [30,34,37,49–51]. As confirmed by X-ray structural analysis, the compounds [TpReCl$_2$(py)], [TpReCl(OPh)(py)] and [(pzTp)ReCl$_2$(PEt$_2$Ph)] are six-coordinate, displaying an octahedral coordination geometry, with facial and symmetrical coordination of the κ^3-Tp′ ligand. This symmetrical coordination is different from what is observed in the analogous Re(V) oxo complexes, where exists a strong *trans* influence of the oxo group [21,34,49].

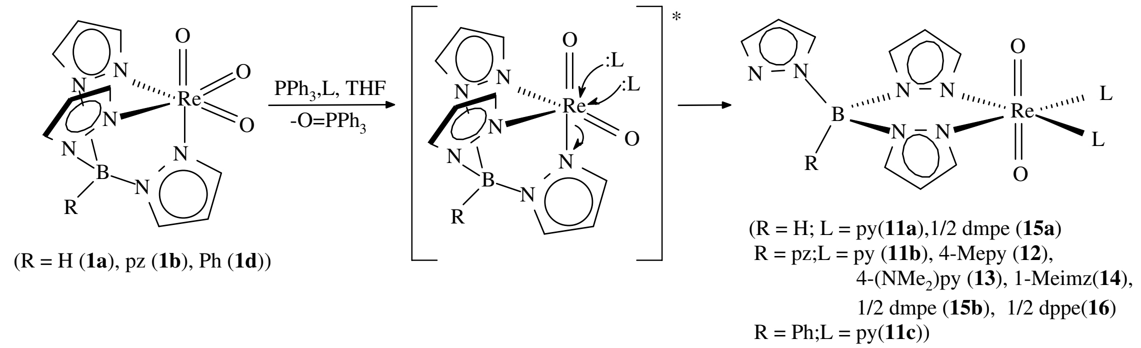
Mayer et al. described the first *cis*-[TpReO$_2$X] compounds (X = Cl (**18a**), Br (**18b**), I (**18c**)) obtained by oxidation of oxotriflates with a stoichiometric amount of pyridine *N*-oxide (Scheme 19). On the basis of electronic arguments, the *trans* configuration would be more stable for these d^1-dioxocomplexes, but the facial disposition imposed by the κ^3-Tp is certainly responsible



Scheme 12.



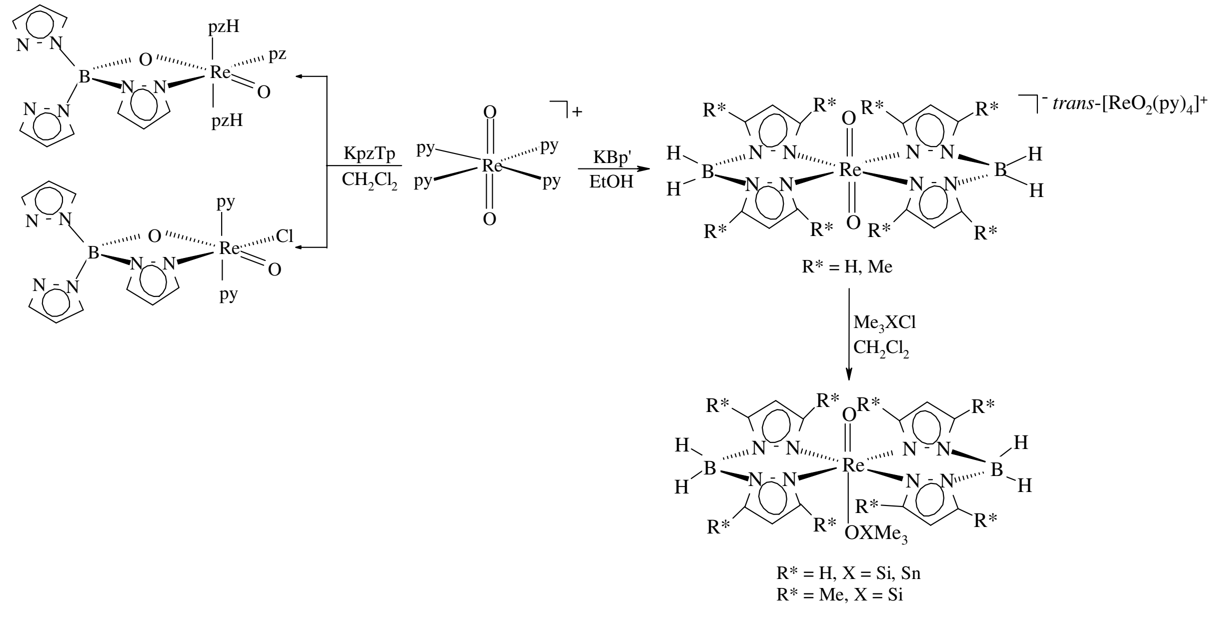
Scheme 13.



(R = H (**1a**), pz (**1b**), Ph (**1d**))

(R = H; L = py(**11a**),1/2 dmpe (**15a**)
R = pz;L = py (**11b**), 4-Mepy (**12**),
4-(NMe$_2$)py (**13**), 1-Meimz(**14**),
1/2 dmpe (**15b**), 1/2 dppe(**16**)
R = Ph;L = py(**11c**))

Scheme 14.

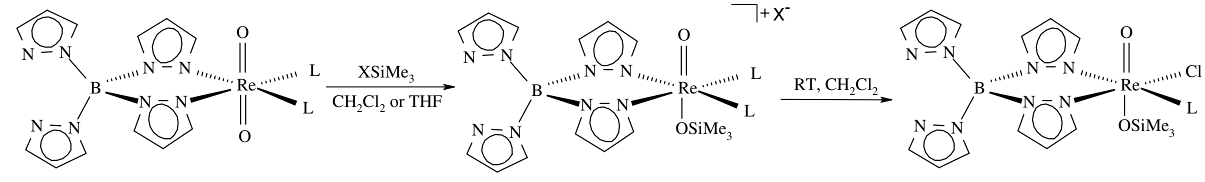


R* = H, Me

R* = H, X = Si, Sn
R* = Me, X = Si

+
trans-[ReO$_2$(py)$_4$]Cl

Scheme 15.



(L = py (**11b**), 4-(NMe$_2$)py (**13**), 1-Meimz (**14**),
1/2 dmpe (**15b**)

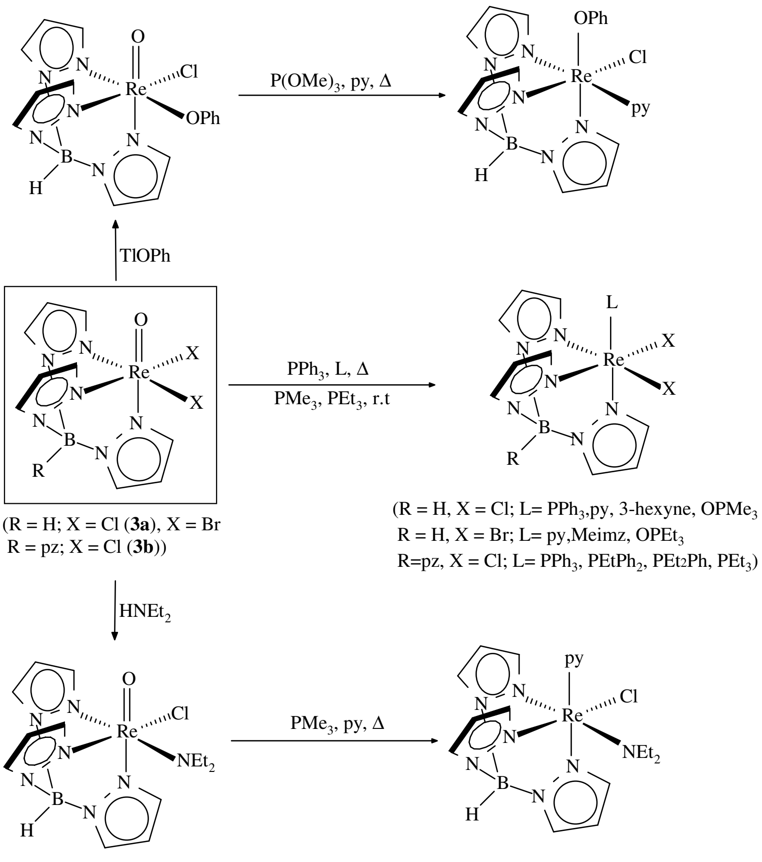
(X = Cl, L = py, 4-(NMe)$_2$py, 1-Meimz,
1/2 dmpe; X = I, L = py)

(L = py, 4-(NMe)$_2$py, 1-Meimz)

Scheme 16.

for the formation of this unusual Re(VI) *cis*-dioxo complexes [23]. The paramagnetic nature of compounds **18** results in very broad and uninformative ^{1}H NMR resonances, but the X-ray structural analysis of **18a** demonstrated that the two oxo ligands are in a *cis*-arrangement, with the homoscorpionate ligand coordinating in a tridentate and facial way. The Re–O bond lenghts of 1.797(11) and 1.741(10) Å are longer than the typical Re–O triple bonds (1.69(3) Å), but compare well with the Re–O bond distances found in *trans*-dioxo complexes (ca. 1.76(2) Å) [8,45–47]. Compounds **18** are not particularly reactive, being fairly air stable and only slightly water sensitive. As solids or in solution, *cis*-[TpReO$_2$X] (**18**) slowly disproportionate to [TpReO$_3$] (**1a**) and [TpReOX$_2$] [23].

The formation of 18 was considered to go through cationic Re(VII) intermediates [TpReO$_2$X]$^+$ (X = Cl, Br, I), which undergo rapid one electron reduction [23].



(R = H; X = Cl (**3a**), X = Br
R = pz; X = Cl (**3b**))

(R = H, X = Cl; L= PPh$_3$,py, 3-hexyne, OPMe$_3$
R = H, X = Br; L= py,Meimz, OPEt$_3$
R=pz, X = Cl; L= PPh$_3$, PEtPh$_2$, PEt$_2$Ph, PEt$_3$)

Scheme 17.

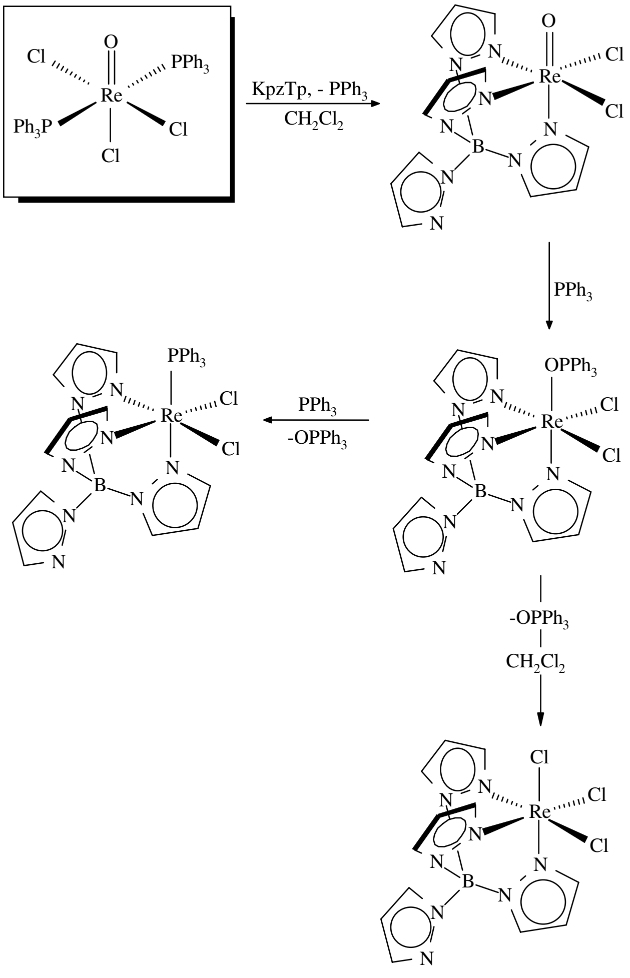
Mayer and coworkers [10,31,32,44] also claimed that the related Re(VII) dioxo cations $[Tp'ReO_2Y]^+$ ($Tp' = Tp$, Tp*; Y = aryl, alkyl, hydroxyde, alkoxide) are the key reactive species in the reactions of $[TpReO(OR')_2]$ or [Tp′ReOY(OTf)] with py-O and Me_2SO. The fate of the strongly electrophilic $[Tp'ReO_2Y]^+$ cations, which were never isolated, is quite dependent on the nature of the co-ligands. Alkoxides, alkyl and hydroxy complexes are in general oxidized by py-O or Me_2SO to $[Tp'ReO_3]$ and to the corresponding aldehydes or ketones [10,31,44]. The exception is the oxidation of [Tp*ReO(OTf)(Et)] with Me_2SO, which is not accompanied by release of the expected acetaldehyde [10].

During studies of the oxidation of [Tp′ReO(Ph)OTf] (Tp′ = Tp, Tp*) with Me_2SO or pyridine *N*-oxide, Mayer and coworkers [10,32] reported the first clear examples of a thermal [1,2]-migration of an aryl group from a metal center to an oxo-ligand (Scheme 20). According to these authors, the phenyl ligand in the Re (VII) intermediates $[Tp'ReO_2(Ph)]^+$ (Tp′ = Tp, Tp*) migrates to a neighbouring oxo group, forming novel rhenium(V) complexes. However, the nature of the final complexes depends on the scorpionate and on the oxygen atom donor. When Me_2SO is used as oxidant, the reactions proceed with formation of the phenoxide complexes [Tp′ReO(OPh)(OTf)] both for the Tp and Tp* systems. By contrast, the oxidation of [TpReO (Ph)OTf] with py-O led to the formation of a phenoxide and a catecholate, while [Tp*ReO(Ph)OTf] yields a complex mixture of products, which does not include [Tp*ReO(OPh)(OTf)] (Scheme 20) [10,32].

Gable and Brown [16] reduced the compounds $[Tp^*ReO_3]$ and $[pzTpReO_3]$ with PPh_3 or $P(OEt)_3$, and evaluated the in situ generated species $\{Tp'ReO_2\}$ (Tp′ = Tp*, pzTp) in catalytic oxygen transfer reactions. For the Tp* system, they found efficient catalytic oxygen transfer from epoxides to the stoichiometric phosphorus reductant with consequent deoxygenation of the epoxyde and formation of the corresponding olefin. The catalytic reaction is stereospecific and proceeds more rapidly with *cis*- vs. *trans*-alkenes. These authors also found that the use of Tp* or pzTp has a significant influence on the rate and efficiency of the catalytic cycle, the rate being severely retarded by the presence of pzTp. The higher rate of epoxide deoxygenation achieved with Tp* was considered to be due to the larger steric bulk of Tp*, which disfavor dimerization of the catalytically active $\{Tp^*ReO_2\}$ species [16].

2.2.5. Photochemical reactions

Photochemical activation of the complex [TpReO-(C_2O_4)] (**8**), by irradiation with UV light, induces reac-



Scheme 18.

tivity towards different substrates (Scheme 21) [33,52]. The authors considered the photochemical process taking place through the reactive transient {TpReO} and with release of CO$_2$ and CO. The trapping of the intermediate {TpReO} by oxidants like DMSO, CHCl$_3$ and phenanthrenequinone, yielded stable rhenium(V) or rhenium(VII) products (Scheme 21). The starting oxo-oxalate reacts also with the photochemically generated transient yielding the dimer **19**. The reaction with dioxygen was also studied, and the peroxo {TpReO(η^2-O$_2$)} was formulated as the possible intermediate. This intermediate, which was never isolated, reacts further affording the rhenium(VII) trioxo [TpReO$_3$] [33].

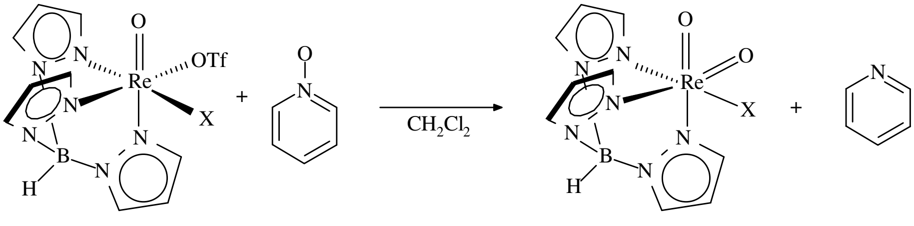
Most of the Re(V) and Re(VII) compounds indicated in Scheme 21 can be obtained either by a photochemical reaction or by a chemical pathway. However, the metallacycle [TpReO(C$_9$HF$_{12}$NO$_4$)] (**20**) can only be prepared by photolysis of **8**. The formation of **20** results from a condensation of two (CF$_3$)$_2$C=O molecules and one CH$_3$CN molecule [52].

Photolysis of [TpReO(Cl)I] (**5**) or [TpReOI$_2$] (**6**) in aromatic hydrocarbons promotes C–H activation of the solvents giving the oxo aryls [TpReOCl(Ph′)] or [TpReO(Ph′)$_2$] (Scheme 22). At least one iodide ligand appears to be needed for arylation, as [TpReOCl$_2$] (**3a**) is unreactive [22].

Another interesting result, and a quite rare process in the chemistry of metal transition complexes, is the formation of Re alkoxides by photochemical aryl-to-oxo and alkyl-to-oxo migration in [TpReOCl(Ph)] and [TpReOCl(Et)], respectively. For the phenyl derivative the type of isolated products depends on the reaction conditions (Scheme 23) [22,49]. In the absence of coordinating substrates, photolysis of [TpReOCl(Ph)] in benzene yields two new paramagnetic compounds tentatively assigned as the two diastereomers of the asymmetric [{TpRe(OPh)Cl}(μ-O){TpRe(Ph)(Cl)}] (Scheme 23) [49]. Photolysis in neat CH$_3$CN or in benzene solutions containing pyridine or Me$_3$PO produce the paramagnetics adducts [TpReCl(OPh′)(L)] (L = CH$_3$CN, Me$_3$PO, py) (Scheme 23), while photolysis in the presence of Me$_2$SO proceeds with formation of a diamagnetic oxo-phenoxide [TpReOCl(OPh)], due to oxygen atom transfer from Me$_2$SO. Mechanistic studies showed that the phenyl to oxo migration occurs predominantly via an intramolecular [1,2]-shift. Mayer and coworker [49] also reported that photolysis of the oxo alkyl [TpReOCl(Et)], in the presence of pyridine, gave [TpReCl(OEt)(py)], but the net ethyl migration seems to involve free ethyl radicals.

2.3. Hydrides and oxo-hydrides

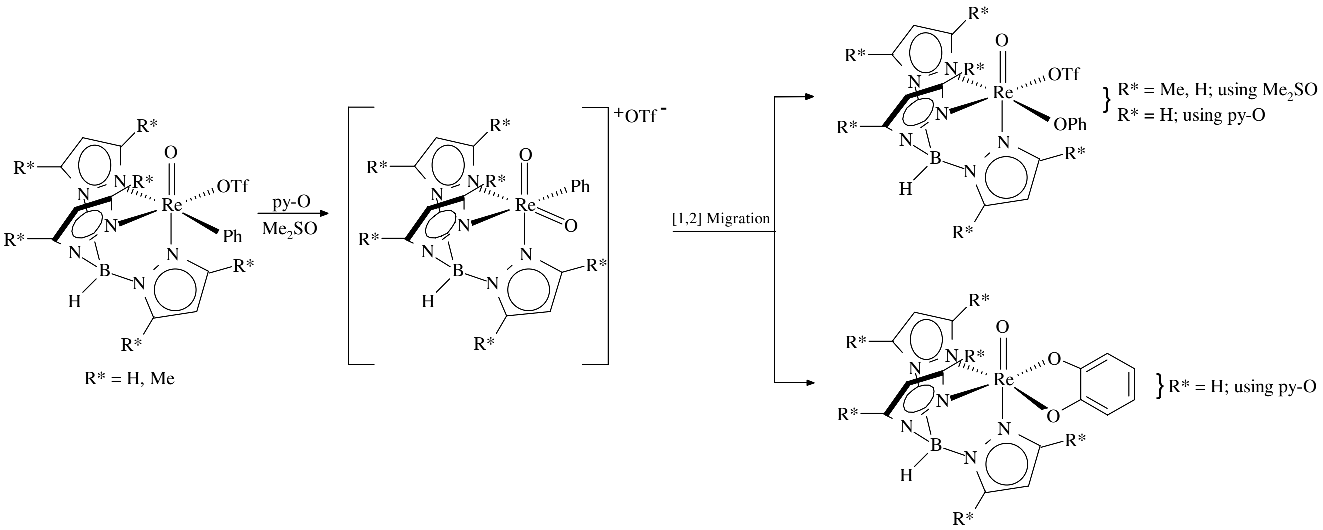
Crabtree et al. [53] reported the complexes [TpReH$_6$] and [TpReH$_4$(PPh$_3$)] which were prepared by reacting LiAlH$_4$ with [TpReOCl$_2$] (**3a**) and



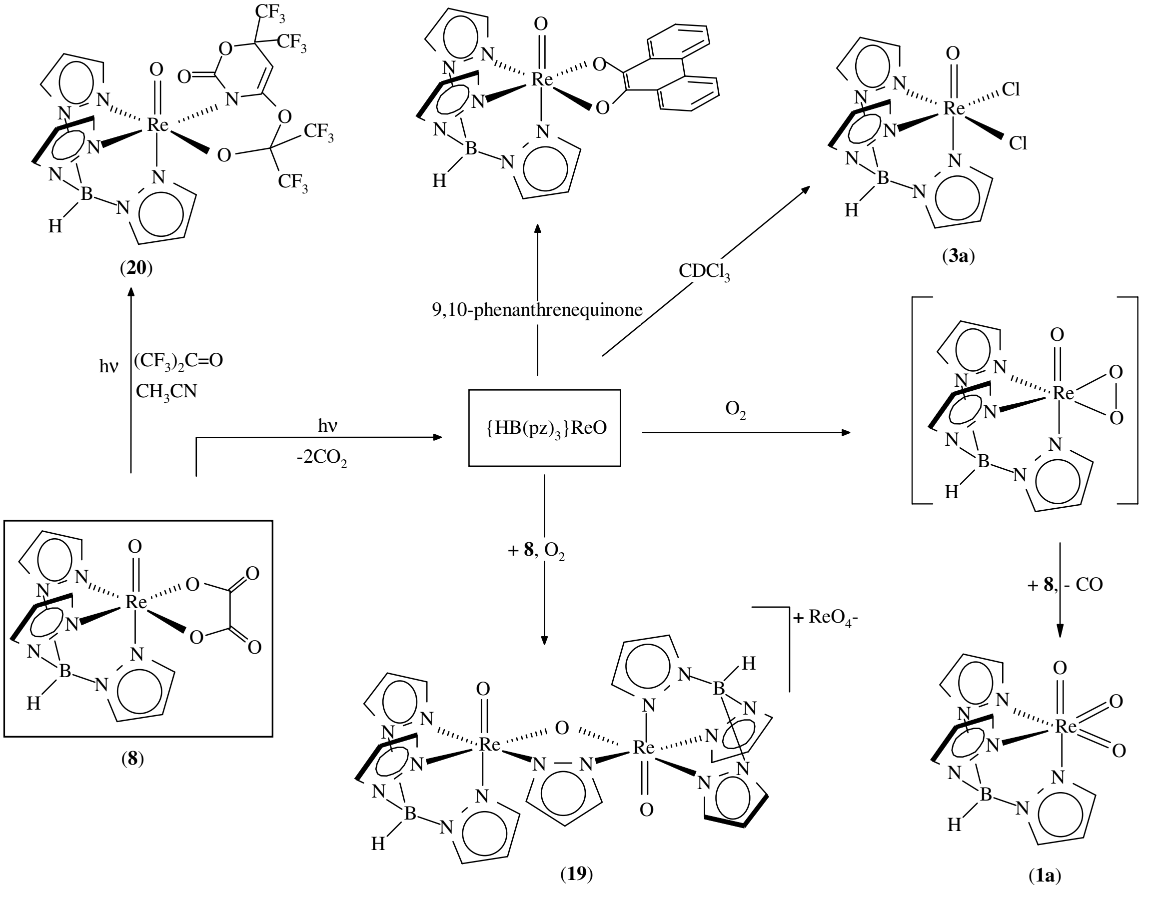
(X = Cl, Br, I)

(X = Cl (**18a**), Br (**18b**), I (**18c**))

Scheme 19.



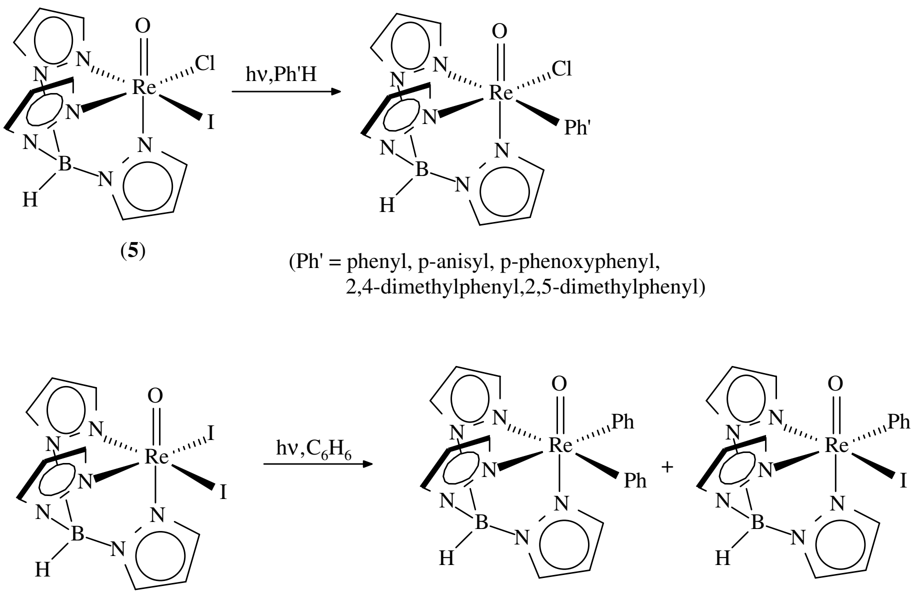
Scheme 20.



Scheme 21.

[TpReCl$_2$(PPh$_3$)], respectively. Based on T_1 and $J_{H–D}$ measurements, a classical character has been proposed for both hydrides.

Santos et al. described a novel route for preparing Re(III) (**21**) and Re(V) (**22**) hydride complexes, which is based on the reaction of [ReOCl$_3$(PPh$_3$)$_2$] with heteroscorpionates, using alcohols as the solvent (Scheme 24). These authors also studied the reaction of [ReOCl$_3$(PPh$_3$)$_2$] with Na[Ph$_2$Bp] in methanol. In this case, as expected, no hydrides were formed and, from a mixture of oxocomplexes, it was possible to isolate [ReO(OMe){κ^2-Ph$_2$B(OMe)(pz)}$_2$] [54].

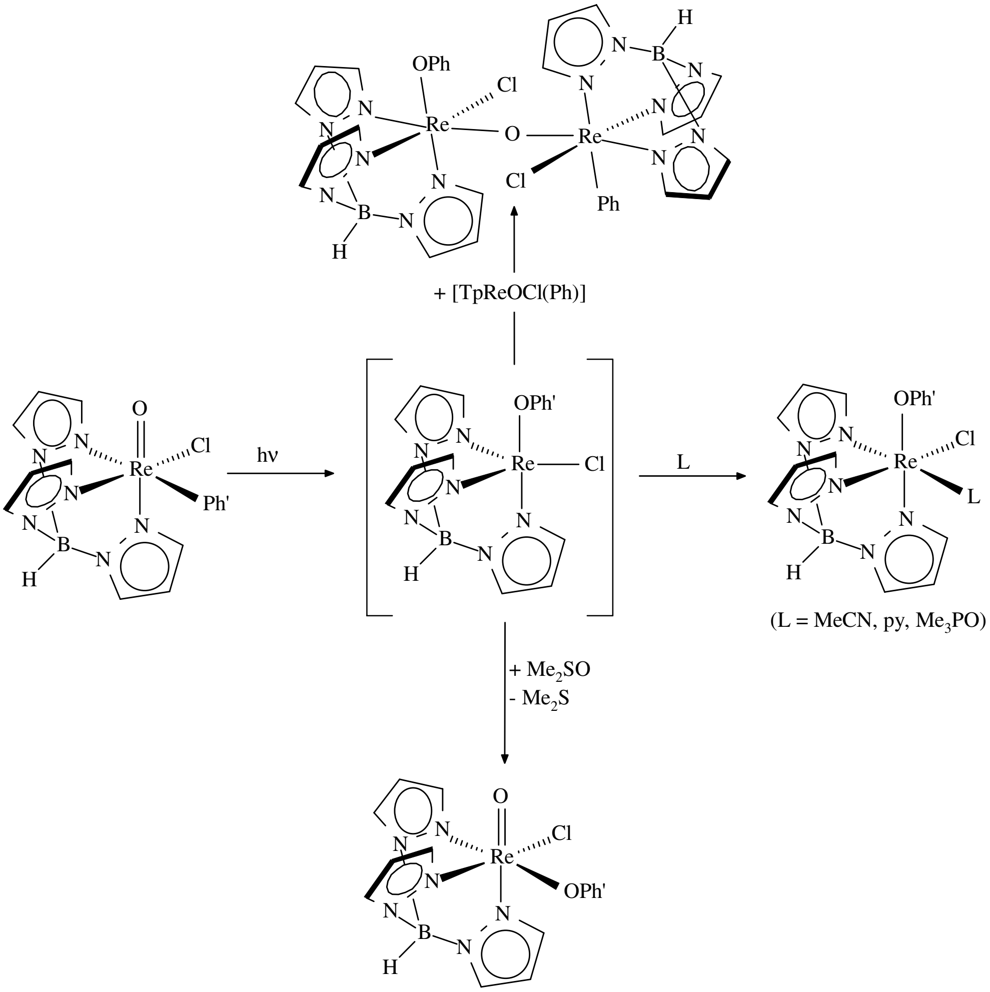


(**5**)

(Ph' = phenyl, p-anisyl, p-phenoxyphenyl,
2,4-dimethylphenyl,2,5-dimethylphenyl)

(**6**)

Scheme 22.



(L = MeCN, py, Me_3PO)

Scheme 23.

The crystal structures of **21a** and **22b** were determined, but the hydride ligands were not located by X-ray. The structural parameters of these hydrides were tentatively assigned by a combination of X-ray diffraction and Molecular Orbital calculations of ab initio and Extended Hückel (EHMO) type [54]. The structures of **21a** and **22b** are the first examples of Re(III) and Re(V) hydrides anchored by asymmetric heteroscorpionates, coordinated in a κ^3-(*N*,*N*,*O*) fashion. The spectroscopic, structural and theoretical studies performed on **21** and **22** indicated a classical character for these hydrides [54].

Recently, Mayer and coworkers [55] reported the quite unusual oxo-hydrides [Tp*ReO(H)Cl] (**23**), [Tp*ReO(H)$_2$] (**24**) and [TpReO(H)Cl] synthesized by reacting [Tp*ReO(OMe)Cl], [Tp*ReO(OMe)$_2$] or [TpReO(OEt)Cl] with $BH_3 \cdot THF$ in toluene at low temperatures (Scheme 25). Prolonged reactions of [Tp*ReO(OR′)$_2$] (R′ = OMe, OEt) with excess $BH_3 \cdot THF$ afford Tp*ReH$_6$ as the only isolable rhenium product [10].

Complex **23** yields [Tp*ReO(H)(OTf)] (**25**) by metathesis with AgOTf in benzene/CH_2Cl_2 [10,55]. Compound **25** is six-coordinate and displays a distorted octahedral coordination geometry, with the hydride ligand in one of the octahedral sites (Re–H, 1.69 Å) [10].

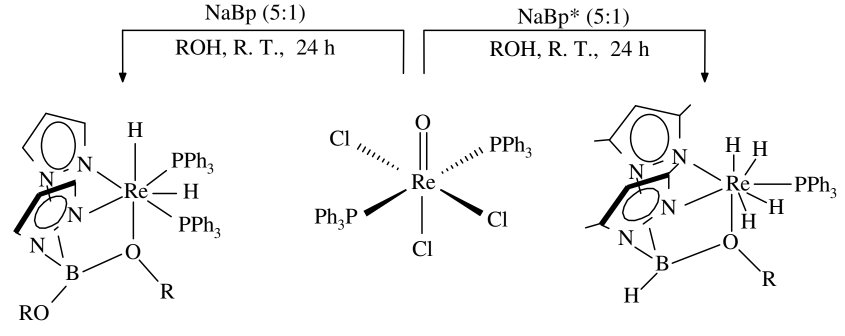
Compound **25** reacts with $CDCl_3$, acetaldehyde, ethylene and propylene affording [Tp*ReO(Cl)(OTf)], [Tp*ReO(OEt)(OTf)], [Tp*ReO(CH_2CH_3)(OTf)] and [Tp*ReO($CH_2CH_2CH_3$)(OTf)], respectively [10]. The triflate ligand in **25** is easily displaced by pyridine yielding the cationic compound [Tp*Re(O)H(py)][OTf]. This cation is also formed, together with [Tp*ReO$_3$] (**1c**), when **25** is treated with pyridine *N*-oxide. Using Me$_2$SO as the oxygen atom transfer reagents, **25** is oxidized mainly to [Tp*ReO$_3$]. By analogy with phenyl-to-oxo migrations, the mechanism proposed for these oxidation reactions involves a [1,2]-migration of the hydride to an oxo ligand in [Tp*ReO$_2$H]$^+$, via the intermediate [Tp*Re(O)(OH)(OTf)], which is further oxidized to **1c**.

2.4. Carbonyl complexes

In the late 1960, the tricarbonyl compounds [Tp′Mn(CO)$_3$] (Tp′ = Tp, pzTp) were the first reported group 7 scorpionate complexes [56,57]. Subsequently, several research groups extended the chemistry of homoscorpionate tricarbonyl complexes to Tc and Re. The structurally characterized [Tp′M(CO)$_3$] (M = Tc, Re; Tp′ = Tp*, Tp) were synthesised by reaction of the starting materials [M(CO)$_5$Br] or [M(CO)$_4$(μ-Cl)]$_2$ with the sodium or potassium salts of the correspondent Tp′ ligands [58–60]. The tridentate and facial coordination of the scorpionates, and the facial arrangement of the CO ligands are common structural features of the [Tp′M(CO)$_3$] (M = Mn, Tc, Re; Tp′ = Tp, Tp*) complexes [60].

By contrast, the chemistry of group 7 heteroscorpionate carbonyl complexes is much more limited, being almost restricted to [BpM(CO)$_3$(pzH)] (M = Mn, Re) [61]. In these compounds, the three CO ligands are facially coordinated and the three remaining coordination sites are occupied by the bidentate dihydrobis(pyrazolyl)borate and a pyrazole, arising from partial fragmentation of the Bp ligand [61]. Interestingly, a similar reaction with Na[H$_2$B(tim^{Me})$_2$], a soft congener of Bp, yields almost quantitatively a tricarbonyl complex with the heteroscorpionate coordinating through the two thione sulfurs and one robust agostic B–H···Re interaction [62].

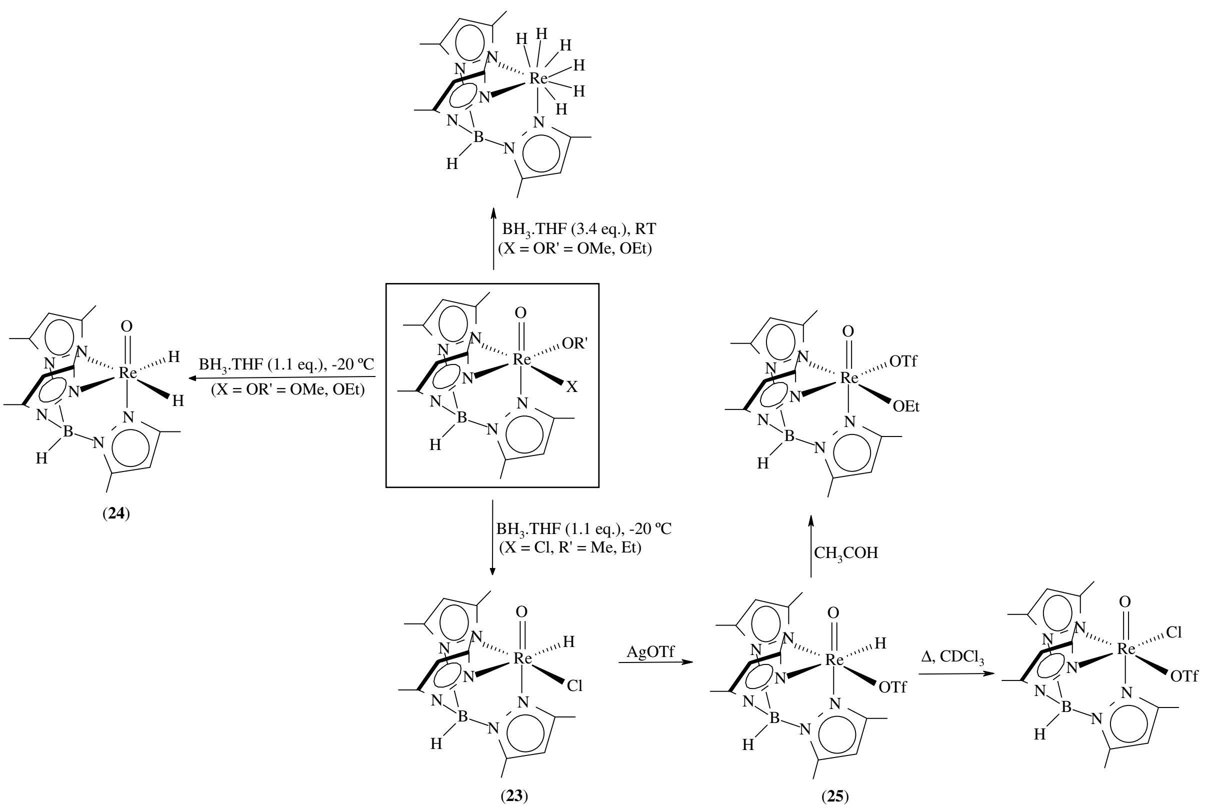
Ultraviolet irradiation of complexes [Tp′M(CO)$_3$] (M = Mn, Tc, Re) in THF led to the adducts [Tp′M(CO)$_2$(THF)] [59,63,64]. In these complexes, the THF ligand is quite labile and easily replaced by other donors with formation of compounds of general formula [Tp′M(CO)$_2$(L)] (M = Mn, Tc, Re) (Scheme 26) [59,63,64]. Complexes [Tp′M(CO)$_2$(THF)] (M = Tc, Re) react also with N$_2$ forming the dinuclear species [Tp′M(CO)$_3$]$_2$(μ-N$_2$) (M = Tc, Tp′ = Tp*; M = Re, Tp′ = Tp) (Scheme 26) [66,67]. Complex [Tc(κ^3-



(R = Me(**21a**), Et (**21b**))

(R = Me(**22a**), Et (**22b**))

Scheme 24.



Scheme 25.

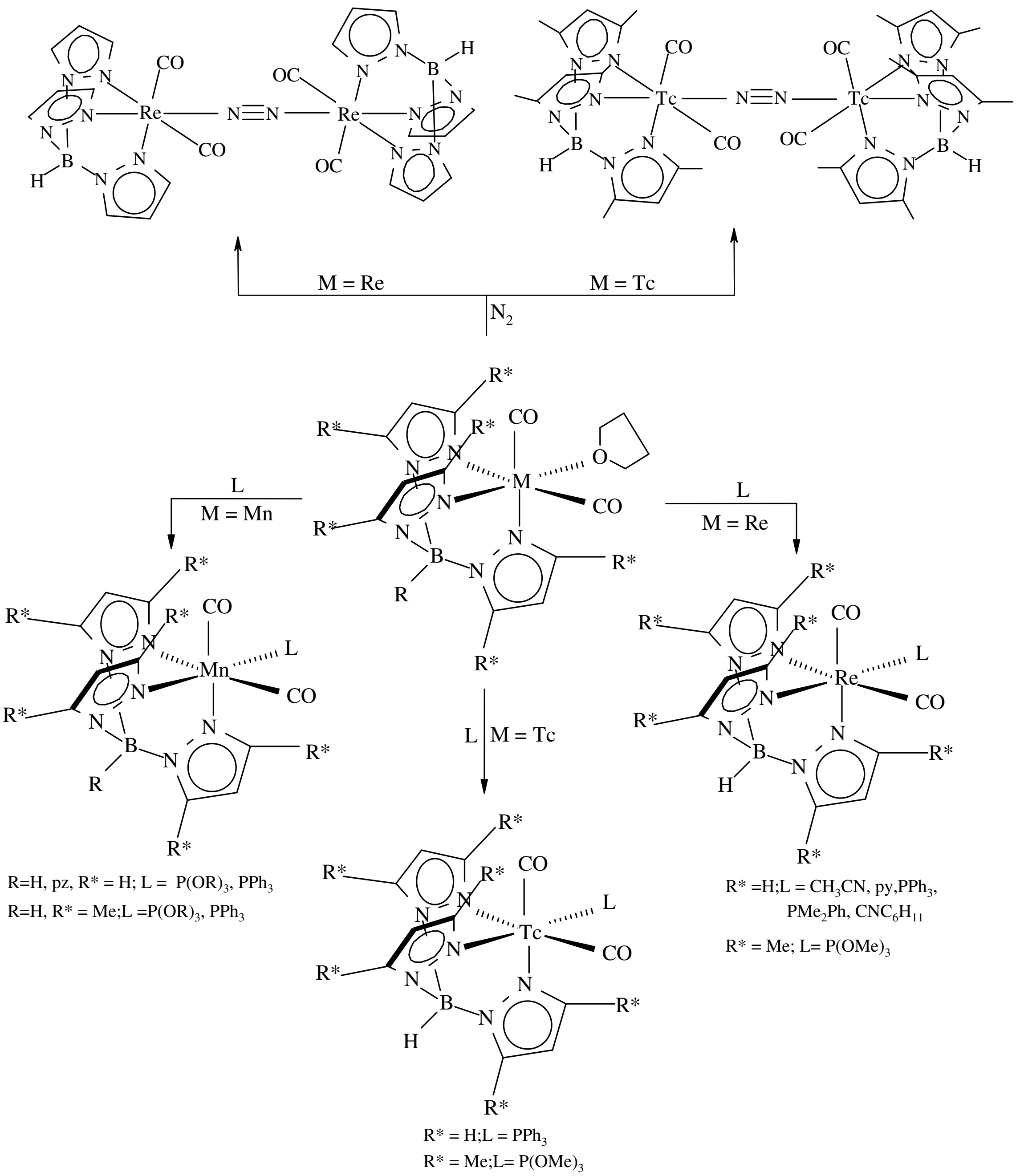
Tp)(CO)$_2$(PPh$_3$)] was alternatively prepared by a metathesis reaction of [TcCl(CO)$_2$(PPh$_3$)$_2$] with KTp [65].

The monomeric di(carbonyl) complexes [Tp′M(CO)$_2$-(L)] (M = Mn, Tc, Re) are six-coordinate, and present an approximately octahedral coordination geometry. The most relevant structural parameter is the shortening of the M–N bond *trans* to the neutral co-ligand (L = THF, PR$_3$, P(OR)$_3$) [59,64,65]. The dinitrogen-bridged bimetallic complexes [Tp′M(CO)$_3$]$_2$(μ-N$_2$) (M = Tc, Tp′ = Tp*; M = Re, Tp′ = Tp) were also structurally characterized, and a different orientation for the scorpionates in the Re and in the Tc compounds was found (Scheme 26). These dimers are unique examples of structurally characterized dinitrogen bridged ditechnetium or dirhenium complexes, and the M(μ-N$_2$)M moieties are best described as possessing M–N single and N–N triple bonds [66,67].

Recently, Harman and coworkers studied the reactivity of [TpRe(CO)$_2$(THF)] (**26**) towards unsaturated substrates, namely cyclopentene, furan, thiophene, naphthalene and *N*-methylpyrrole, in order to stabilize monomeric complexes containing η^2-bound aromatic ligands (Scheme 27). The postulated monomeric or dimeric structures for the products, and the coordination mode of the unsaturated substrates were based on IR and NMR spectroscopy [67].

To avoid the dimerization process observed in these reactions, Harman and coworkers replaced one of the CO ligands in the fragment {TpRe(CO)$_2$} by a weaker π-acid or stronger σ-donor ligand. Consequently, the resulting fragments, {TpRe(CO)(L)} (L = ^{t}BuNC, PMe$_3$, NH$_3$, 1-Meimz), were more π-basic and were able to bind a series of aromatic molecules, without undergoing dimerization or oxidative addition reactions (Schemes 28 and 29) [50,68,69]. Among the more π-basic compounds, [TpRe(CO)(1-Meimz)(η^2-C$_6$H$_6$)] (**27**) proved to be remarkably versatile for the direct synthesis of organometallic derivatives with a variety of unsaturated substrates coordinated in a π-fashion to the metal center (Scheme 29). The authors found that, under nitrogen, the rate of dissociation of the dihapto-coordinate aromatic ligand decreases as the fragment becomes more electron-rich, while the stability to air shows a somewhat inverse trend [50,68–73].

X-ray diffraction analysis was performed on the different [TpRe(CO)(L)(η^2-L$_\pi$)] (L = ^{t}BuNC, PMe$_3$, py, NH$_3$, 1-Meimz) complexes [50,69,70]. In all, the coordinate double bond of the aromatic ligand (L$_\pi$) is oriented perpendicular to the rhenium carbonyl bond, in order to optimize π-back-bonding. [50,69,70]. Due to their asymmetric character, the [TpRe(CO)(L)(η^2-L$_\pi$)] compounds exist in solution as two diastereomers, which undergo a non-dissociative interconversion (Scheme 30). The author claims that such interconversion occurs via both interfacial and intrafacial migrations. NOE and 2D NMR techniques allowed the

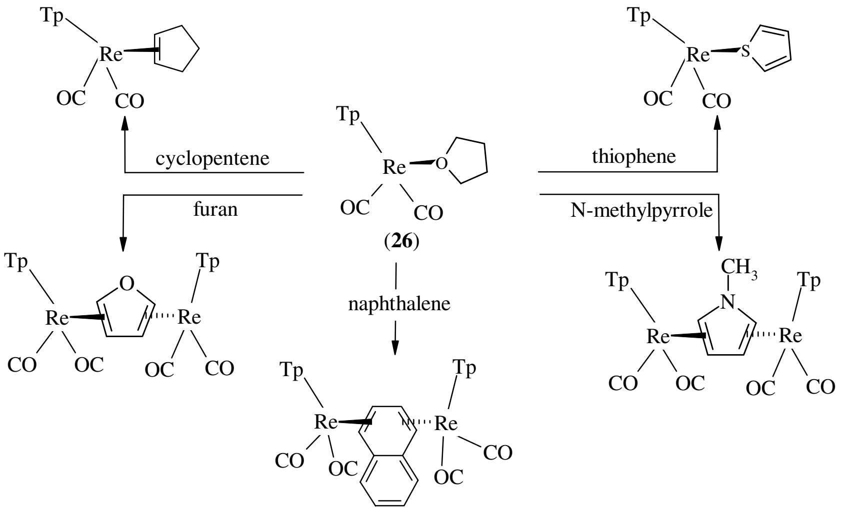


Scheme 26.

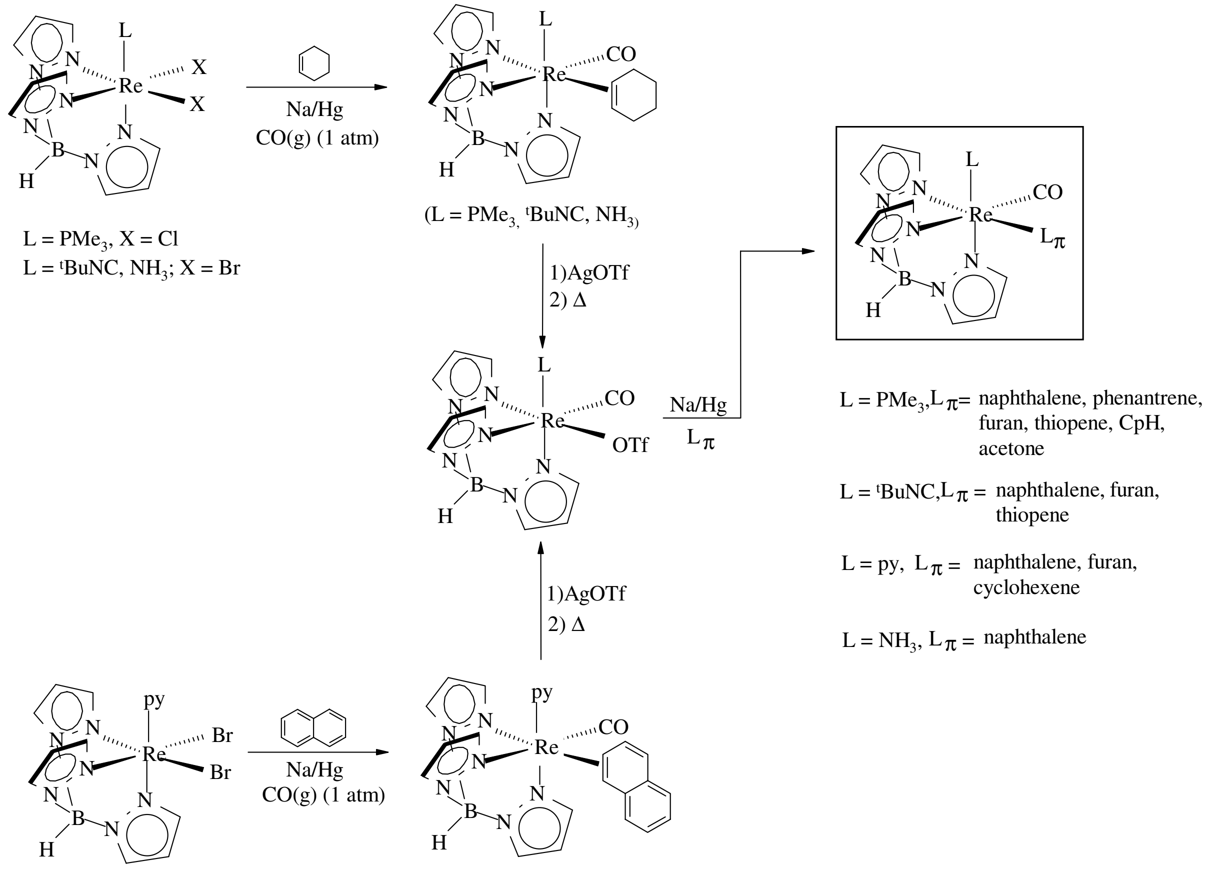
identification of each diastereomer and ^{1}H NMR spin transfer experiments were used to calculate the rate and free energy of activation for the isomerization processes [74]. The diastereoselectivity exhibited by these systems is very much dependent on the nature of the L and L_π ligands, being governed by the relative steric interaction of L and *trans* pyrazole ring with the L_π (Scheme 30).

Due to the volume of PMe_3, a single diastereomer predominates in complex [TpRe(CO)(PMe_3)(η^2-naphthalene)] (**A**, Scheme 30) [50,74]. The resolution of racemic [TpRe(CO)(1-Meimz)(η^2-benzene)] into the *R* and *S* enantiomers was achieved using (*R*)-α-pinene as a chiral auxiliary and based on an elaborated series of redox and substitution reactions [75].

The η^2-coordination of the aromatic substrates to the π-basic metal fragments [TpRe(CO)(L)] is accompanied by the disruption of the aromaticity through π-back-bonding. For example, the crystal structure of [TpRe(CO)(1-Meimz)(η^2-benzene)] (**27**) shows dearomatization to such an extent that the uncoordinated portion of the benzene ring closely resembles cyclohexadiene [70]. This dearomatization explains why **27** undergoes a



Scheme 27.



L = PMe$_3$, L$_\pi$ = naphthalene, phenantrene, furan, thiopene, CpH, acetone

L = ᵗBuNC, L$_\pi$ = naphthalene, furan, thiopene

L = py, L$_\pi$ = naphthalene, furan, cyclohexene

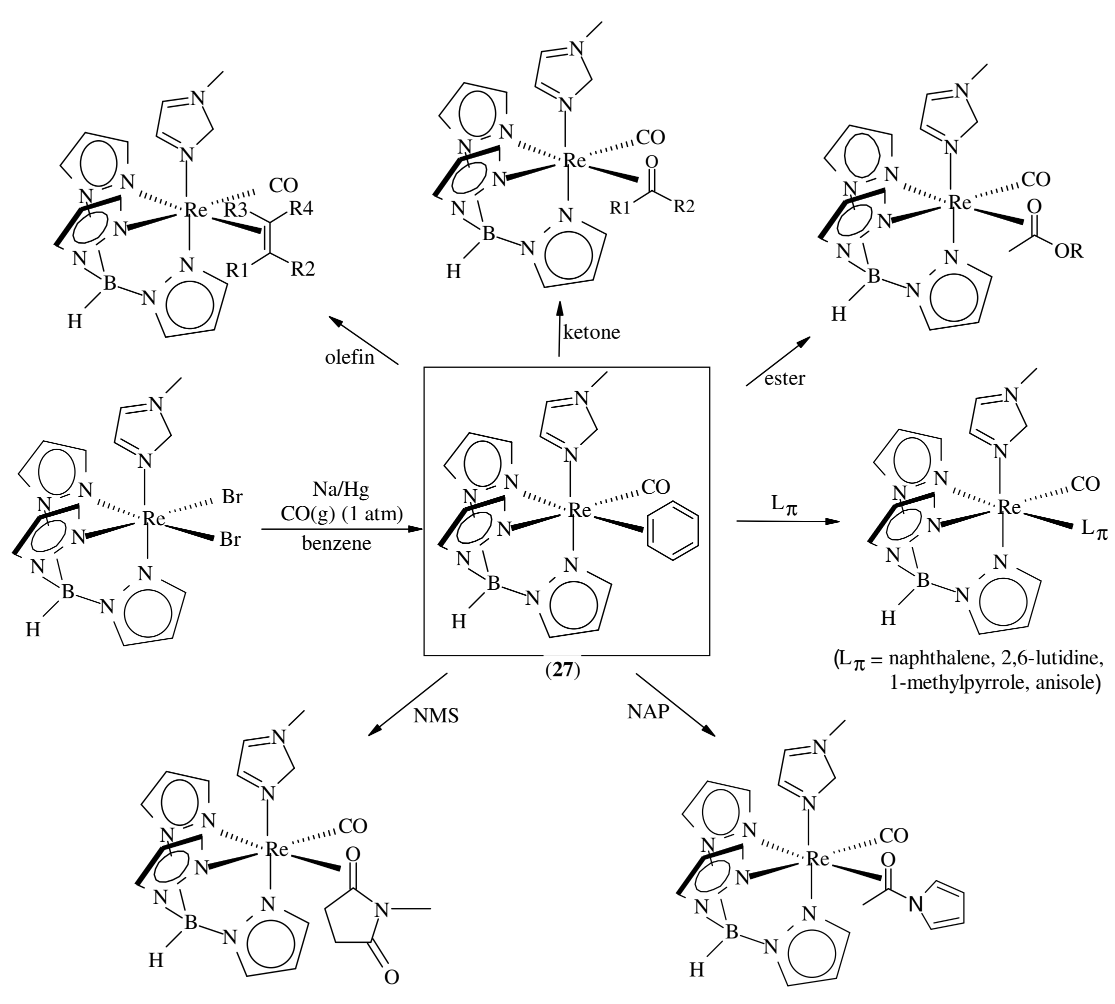
L = NH$_3$, L$_\pi$ = naphthalene

Scheme 28.

Diels-Alder cyclo-addition with *N*-methylmaleimide (NMM) with a specific rate that is 60% faster than that observed for cyclohexadiene (Scheme 31) [76].

X-ray crystallographic analysis of the complex from the cyclo-addition process, **28**, confirmed that the reaction occurs exclusively at the arene face non-coordinated to the metal with exclusive *endo* selectivity. Oxidation of the metal center promotes decomplexation with liberation of bicyclo[2.2.2]-octadiene and/or octenone products, depending on the oxidation conditions (Scheme 31) [76].

Coordination of furans to the fragments {TpRe(CO)(L)} (L = ᵗBuNC, PMe$_3$, 1-Meimz) activates these heterocycles towards cycloaddition reactions with dif-

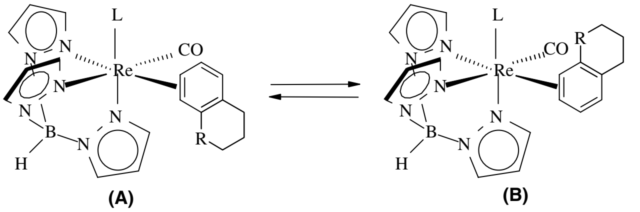


(Lπ = naphthalene, 2,6-lutidine, 1-methylpyrrole, anisole)

Scheme 29.

ferent dienophiles. When the furan is bound through the 4,5-positions it undergoes [2 + 2] cyclizations, while [3 + 2] cycloaddition reactions occur when the heterocycle is bound through the 3,4-positions [77].

The acid-catalysed addition of methanol to the coordinated furan in complexes [TpRe(CO)(L)(η^2-furan)] (L = ^{t}BuNC, PMe$_3$, py, 1-Meimz) was also evaluated. In traditional organic reactions methanol attacks at the 3-position of furan, but in these Re(I) systems the reactions occur at the 2-position, and two diastereomers of η^2-coordinated 2-methoxy-2,3-dihydrofurans are formed (Scheme 32) [78].



Scheme 30.

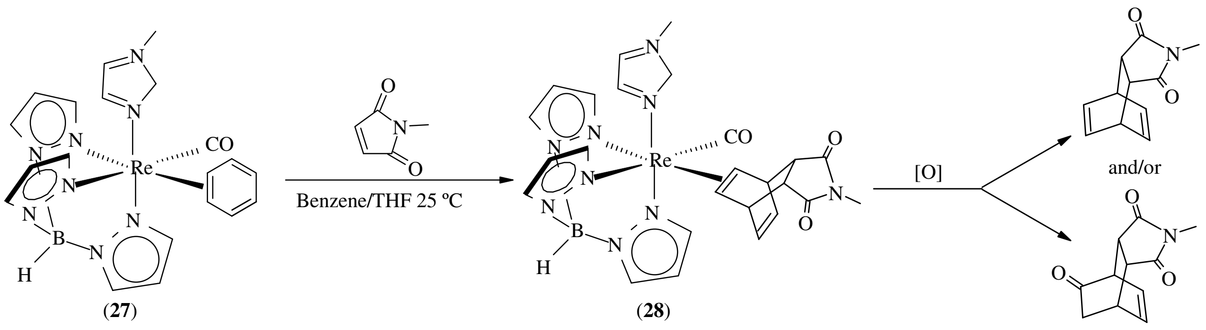
The complexes [TpRe(CO)(L)(η^2-naphthalene)] (L = PMe$_3$, NH$_3$, py, 1-Meimz) undergo tandem electrophilic/nucleophilic addition reactions, by sequential treatment with triflic acid and a siloxypropene derivative, leading to 1,4- or 1,2-addition products (Scheme 33) [79]. The regioselectivity of these reactions depends on the nature of the co-ligand L. The key for the regiocontrol seems to be the formation of single 1H-naphthalenium intermediates and its orientation relatively to the CO bond, as depicted in Scheme 33. The PMe$_3$ complex promotes predominantely the 1,4-addition products, while all the other favor the 1,2-addition [79].

3. 5f-Element scorpionate complexes

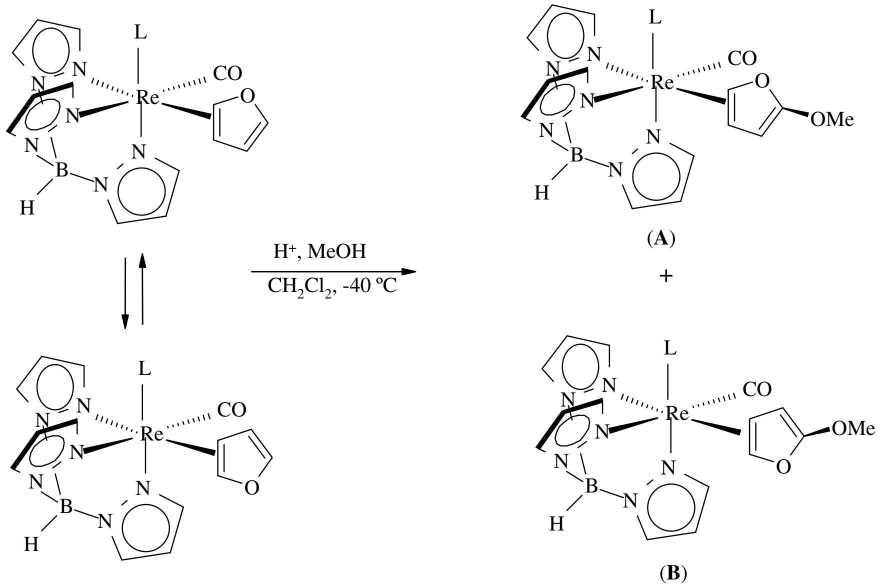
3.1. Trivalent complexes

3.1.1. Bis- and mono-homoscorpionates

The unique and fully characterized Pu complex is the dimer [PuCl(μ–Cl)(κ^3-Tp*)(Me$_2$pzH)]$_2$, which has been isolated in good yield by reacting PuCl$_3$ and NaTp*, in



Scheme 31.



	A:B
L = ᵗBuNC	1:2
PMe_3	2:1
py	1:1
1-Meimz	1:3

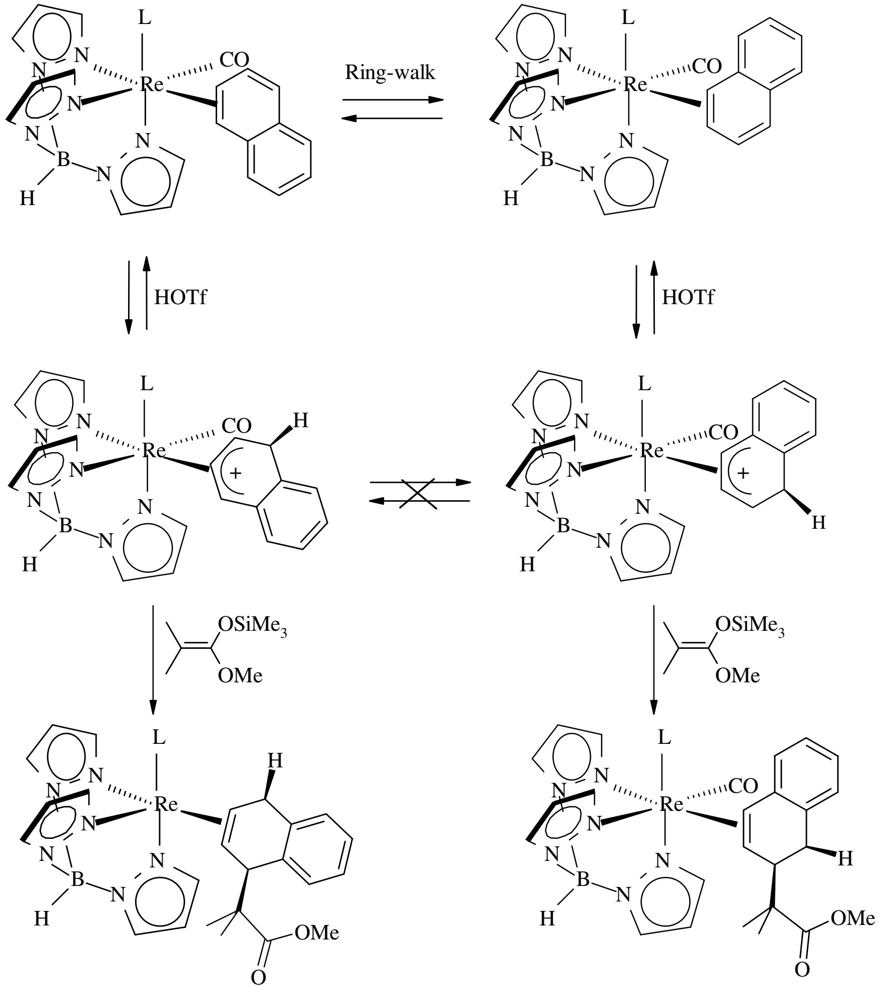
Scheme 32.

refluxing THF during 2 weeks. The synthesis of another plutonium(III) compound, [$PuTp_3$], was also mentioned, but no details were given [2,80].

Bis- and mono-Tp* U(III) complexes have been synthesized by metathesis of [$UI_3(THF)_4$] or [$UCl_3(THF)_x$] in THF (Scheme 34). The iodide derivatives [(κ^3-Tp*)$_2$UI] (**29**) and [(κ^3-Tp*)$UI_2(THF)_2$] (**30**) were fully characterized, including X-ray crystallographic analysis [81,82]. The chloride compound was never characterized in the solid state and its formulation was based on spectroscopic data, as well as on the reactivity towards unsaturated substrates (Scheme 34) [83,84].

Compound **29** readily undergoes iodide abstraction with $TlBPh_4$ to form [(κ^3-Tp*)$_2$U(THF)] [BPh_4] (**31**) [81]. This cation is stable in the solid state but tends to decompose in THF solution. X-ray structural characterization of **29**, **30** and **31** showed that these compounds are seven-coordinate, displaying a distorted capped octahedral coordination geometry. An interesting feature in **29** is the different coordination mode of the two Tp* ligands: one ligand binds normally through three nitrogen atoms, while the other contains one pyrazolyl ring bonded to uranium through both of its nitrogen atoms [82,85].

Takats et al. demonstrated the utility of [(κ^3-Tp*)$UI_2(THF)_2$] as precursor for further derivatization, and by metathesis [(κ^3-Tp*)U{$N(SiMe_3)_2$}I], [(κ^3-Tp*)U{$N(SiMe_3)_2$}$_2$], [(κ^3-Tp*)U{$N(SiMe_3)_2$}{$CH(SiMe_3)_2$}] and [(κ^3-Tp*)U{$CH(SiMe_3)_2$}$_2$(THF)] were synthesized. The



1,4-addition **1,2-addition**

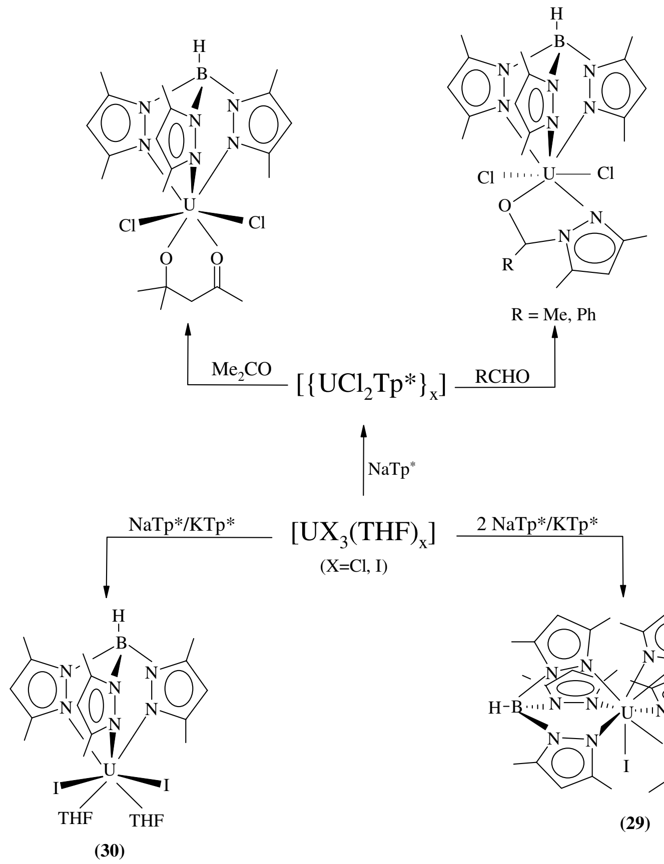
Scheme 33.

bis-amido, bis-alkyl and mixed amido-alkyl derivatives are five- or six-coordinate, displaying trigonal bipyramidal and distorted octahedral coordination geometries [85]. In contrast to [(κ^3-Tp*)U{N(SiMe$_3$)$_2$}I], compounds [(κ^3-Tp*)U{N(SiMe$_3$)$_2$}$_2$] and [(κ^3-Tp*)U{CH(SiMe$_3$)$_2$}$_2$(THF)] are thermally unstable in solution and the decomposition process is solvent dependent [85].

Taking advantage of the possibility of introducing different substituents in the 3-position of the pyrazole ring, the podand Tp$^{2\text{-py}}$ ligand has been synthesized. Takats et al. has shown that [UI$_3$(THF)$_4$] reacts with KTp$^{2\text{-py}}$ in the 1:2 ratio in THF yielding the homoleptic [(Tp$^{2\text{-py}}$)$_2$U]I. This complex is 12-coordinate by the six nitrogen atoms of the pyrazolyl rings and by the six nitrogen atoms of the pyridyl groups, displaying an unusual icosahedral coordination geometry [86].

Recently, Santos and coworkers [87] have shown that [UI$_3$(THF)$_4$] reacts with KTp$^{i\text{Pr}2}$ in THF yielding (κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(THF)$_{2-3}$]. This compound is unstable in solution, the main decomposition product being [(κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(Hpz$^{i\text{Pr}2}$)] (**32**) [87a]. Interestingly, when [UI$_3$(THF)$_4$] is treated with KTp$^{i\text{Pr}2}$ in toluene in the presence of other Lewis bases, different from THF, stable mono-Tp$^{i\text{Pr}2}$ complexes can be prepared. These quite robust compounds of general formula [(κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(L)$_x$] (L = OPPh$_3$, $x = 1$; L = bipy, $x = 1$; L = py, $x = 2$; L = Hpz$^{t\text{Bu,Me}}$, $x = 2$) were obtained in relatively high yields (65–75%) (Scheme 35). The compounds [(κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(OPPh$_3$)], [(κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(bipy)], [(κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(py)$_2$] and [(κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(Hpz$^{i\text{Pr}2}$)] are six- or seven-coordinate, depending on the steric bulk of the neutral co-ligand.

The six-coordinate compound [(κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(OPPh$_3$)] displays an octahedral coordination geometry, while the seven-coordinate [(κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(bipy)] and [(κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(py)$_2$] display, respectively, distorted capped octahedral and pentagonal bipyramidal geometries. Initially, [(κ^3-Tp$^{i\text{Pr}2}$)UI$_2$(Hpz$^{i\text{Pr}2}$)] (**32**) was considered as six-coordinate, by the three nitrogen atoms of the κ^3-Tp$^{i\text{Pr}2}$, two iodides and one nitrogen of the Hpz$^{i\text{Pr}2}$. However, a careful analysis of the relevant structural parameters has shown an additional interaction between



Scheme 34.

the metal and one hydrogen atom of one ^{i}Pr(3) of the Tp^{iPr2}. This seven-coordinate compound displays a capped octahedral coordination geometry with the axial position defined by the hydrogen atom of the ^{i}Pr group interacting with the metal (U–H, 3.06 Å) and by the nitrogen atom of Hpz^{iPr2} [87a].

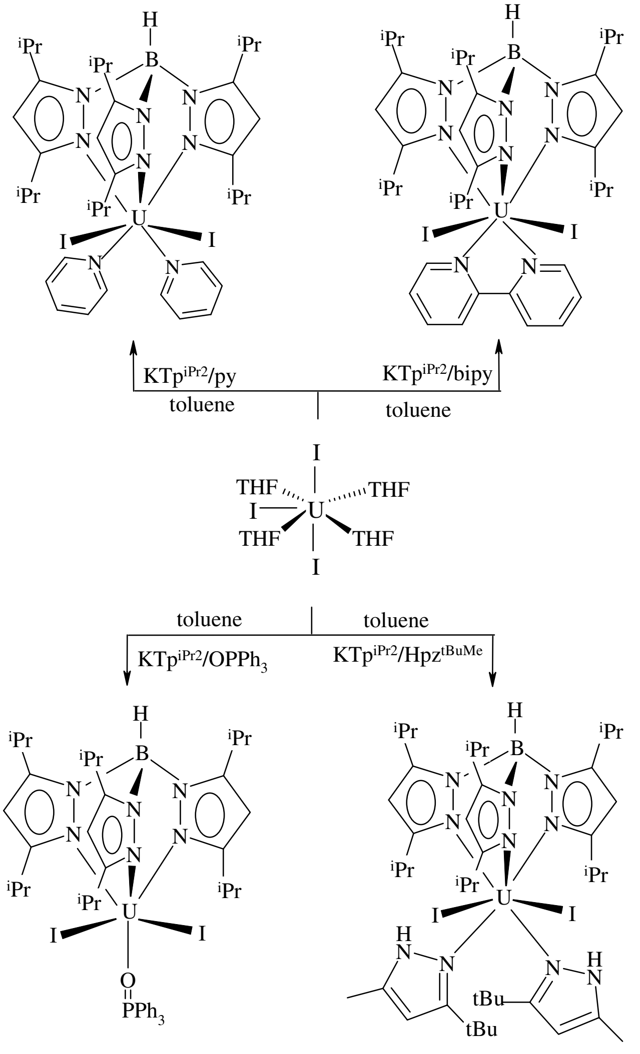
3.1.2. Tris-, mono- and bis-heteroscorpionates

Uranium tricloride or uranium triiodide react with KBp, KBp*, NaPh$_2$Bp and KBp^{iPr2} in a 1:3 ratio yielding [(κ^3-Bp)$_3$U(THF)], [(κ^3-Bp)$_3$U], [(κ^2-Ph$_2$Bp)$_3$U] and [(κ^3-Bp^{iPr2})$_3$U, respectively (Scheme 36) [87–90].

These homoleptic and monomeric compounds present high solubility in toluene and *n*-hexane. In all the six nitrogen atoms of the three ligands are arranged in a trigonal prismatic geometry around the U(III) center. For [(κ^3-Bp)$_3$U(THF)], [(κ^3-Bp*)$_3$U] and [(κ^3-Bp^{iPr2})$_3$U] each of the three rectangular faces of the trigonal prism is capped by an agostic B–H···U interaction, leading in the case of [(κ^3-Bp*)$_3$U] and [(κ^3-Bp^{iPr2})$_3$U] to formally nine-coordinate compounds and in the case of [(κ^3-Bp)$_3$U(THF)] to a 10-coordinated compound, due to the presence of the THF molecule. The [(κ^2-Ph$_2$Bp)$_3$U] compound is six-coordinate by the nitrogen atoms of the three κ^2-Ph$_2$Bp ligands, and displays a trigonal prismatic geometry, with a C_{3h} molecular symmetry. The long U···B distances observed in [(Ph$_2$Bp)$_3$U] (mean value of 3.817 Å) excludes any interaction of the metal with the phenyl groups [90].

Since the bulky and symmetrical substituents in the 3-position of the Bp ligand can be expected to avoid the formation of homoleptic compounds, Santos et al. studied the chemistry of U(III) with KBp^{tBu,Me}. In fact, metathesis of [UI$_3$(THF)$_4$] with KBp^{tBu,Me} in THF yields the first mono-Bp^{tBu,Me} f-element compound [(κ^3-Bp^{tBu,Me})UI$_2$(THF)$_2$] (**33**) (Scheme 36) [90]. In **33** the THF is easily replaced by OPPh$_3$, bipy, Hpz^{tBu,Me} or Hpz^{Me_2}, and the resulting seven-coordinate compounds all retain the agostic B–H···U interaction.

The molecular structure of these "half-sandwich" complexes and their dynamic behavior in solution indicated a metal center relatively unprotected from incoming ligands. Therefore, the possibility of preparing bis-Bp$^{t\text{-Bu},Me}$ complexes was a challenge and has been studied. It was found that [UI$_3$(THF)$_4$] reacts with KBp$^{t\text{-Bu},Me}$ in a 1:2 ratio in toluene yielding the unprecedented [{κ^3-H$_2$B(pz$^{t\text{-Bu},Me}$)(pz$^{Me,t\text{-Bu}}$)}$_2$UI] (**34**). Compound **34** has been formed due to an isomerization of the Bp′ ligand promoted by the metal center [91]. Taking into account that these arrangements are sterically driven processes, this result encouraged the synthesis of the novel asymmetric K[H$_2$B(pz$^{t\text{-Bu},Me}$)(pz^{Me2})]



Scheme 35.

ligand, which was expected to have steric properties adequate for the preparation of bis-$Bp^{R,R^{*\prime}}$ U(III) complexes by metathesis. This has been achieved, and the complex $[\{\kappa^3\text{-}H_2B(pz^{tBu,Me})(pz^{Me_2})\}_2UI]$ (**35**) has been synthesized by metathesis [91]. Compounds **34** and **35** are seven-coordinate by two tridentade asymmetric heteroscorpionates (κ^3-N,N,H) and an iodide ligand, both displaying pentagonal bipyramidal coordination geometries [91]. In these studies, the vulnerability of the scorpionates to fragmentation [2,92] led to the formation of the dimeric compound $[(\kappa^3\text{-}Bp^{tBu,Me})UI(Hpz^{t\text{-}Bu,Me})]_2(\mu\text{-}I)_2$ [91].

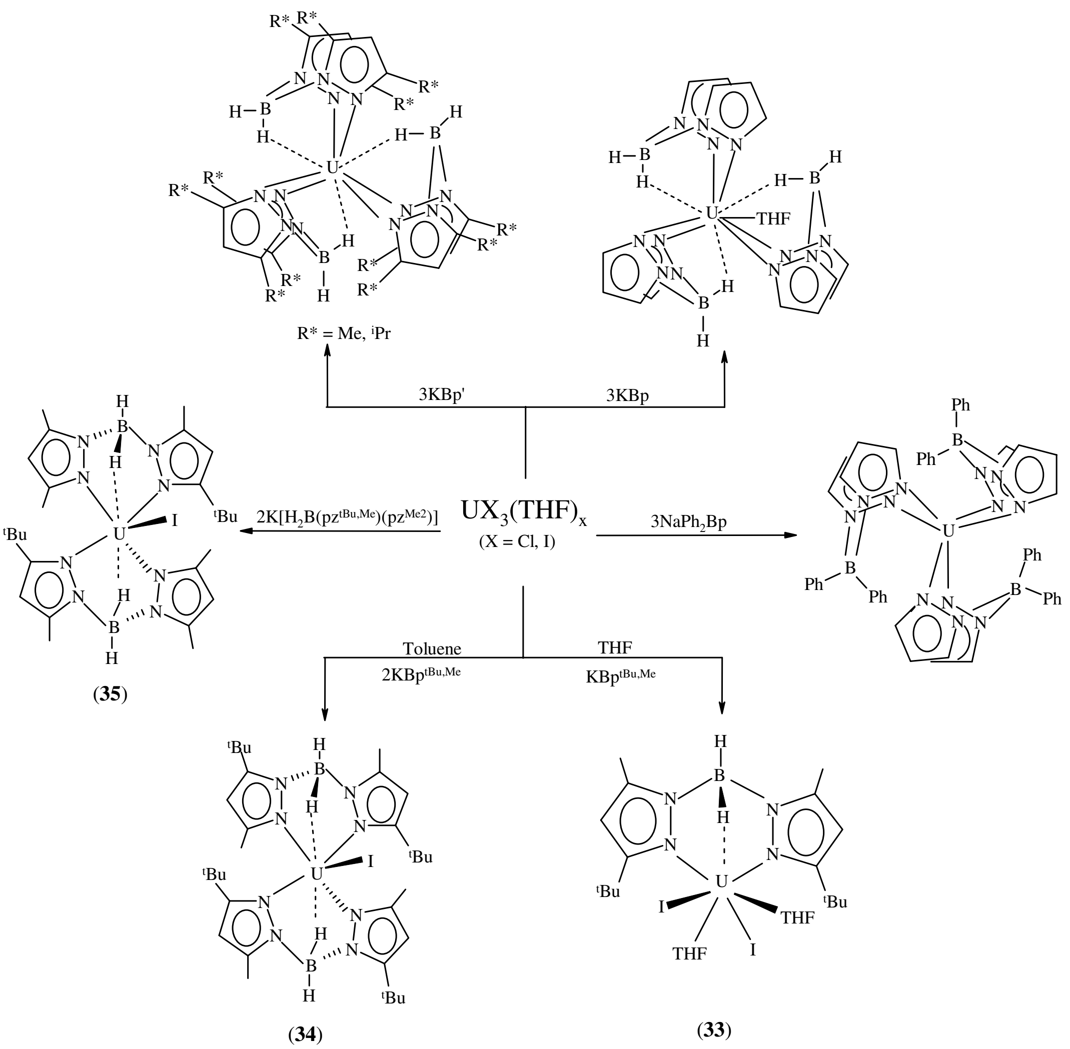
3.2. Tetravalent complexes

3.2.1. Bis and mono-homoscorpionates

The tetrachlorides, MCl_4 (M = Th, U, Np), react with KTp or KpzTp yielding the bis-Tp′ complexes $[(\kappa^3\text{-}Tp)_2AnX_2]$ (X = Cl and An = U, Th, Np; X = Br, An = Th) and $[(\kappa^3\text{-}pzTp)_2UCl_2]$ [4,93]. However, the same type of reaction with bulkier ligands, such as Tp* or Tp^{Ms}, allowed the stabilization of the mono-complexes $[(\kappa^3\text{-}Tp^*)AnCl_3(THF)]$ (An = U, Th, Np) and $[(\kappa^3\text{-}Tp^{Ms^*})UCl_3]$, respectively (Scheme 37) [4,94].

The utility of compounds $[(\kappa^3\text{-}Tp)_2MX_2]$ (M = U, Th, X = Cl; M = U, X = I) and $[(\kappa^3\text{-}pzTp)_2UCl_2]$ for further derivatization has been demonstrated, and several alkyl, amido, thiolate and alkoxide derivatives have been prepared [4,93,95,96]. The reactivity of some U(IV) hydrocarbyl derivatives towards protic substrates, acetone, acetonitrile and iodide was also studied [95,96]. The outcome of the reactions depends on the nature of the alkyl group, as well as on the nature and stoichiometry of the reactants [95,96]. These studies have shown a less rich derivative chemistry for $[(\kappa^3\text{-}pzTp)_2UCl_2]$ than for $[(\kappa^3\text{-}Tp)_2UCl_2]$. In order to get a better insight on these differences, extended Hückel molecular orbital (EHMO) studies have been performed. The analysis of the frontier orbitals did not show any significant differences between Tp and pzTp ligands. However, the calculations indicated that stereochemical interaction affects the reactivity of the complexes stabilized by Tp or pzTp. It was found that the maximum overlap population between these ligands and the uranium metal center is achieved at a bite distance of 3.05 Å for both ligands. This value is ideal for Tp, but for pzTp this distance is energetically unfavorable due to the repulsive interactions between *ortho* hydrogens of the pyrazolyl rings, that are in the same plane. The most favorable bite distance found for the pzTp ligand is 2.85 Å. This feature on its own makes all complexes anchored by pzTp more unstable than their Tp counterparts [93,96]. EHMO calculations provided also some information on the bonding capabilities of the fragment "$[(\kappa^3\text{-}Tp)_2M]$" compared to "$[M(Cp^*)_2]$" and also on the vulnerability of the scorpionate ligands to nucleophilic attack [95].

A significant amount of structural and solution NMR data exists for compounds containing the $[Tp_2'U]$ moiety. In the solid state all are eight-coordinate by two κ^3-Tp′ ligands (Tp′ = Tp, pzTp) and by two monodentate co-ligands, all displaying square antiprismatic coordination geometries, distorted towards bicapped trigonal prism or dodecahedral [4,93,95,96]. In solution all the compounds are fluxional, but static spectra, in accord with the solid state structure, were obtained for most of them, depending on the bulkiness of the co-ligands and/or the coordination number of the metal [4,93,95,96]. For the uranium compounds anchored by pzTp, variable temperature NMR studies revealed that at high temperatures two distinct dynamic processes exist: one intramolecular dissociative process, which promotes the exchange between coordinated and uncoordinated rings, and a non dissociative process involving interconversion of the common eight-coordinate polyhedra (SAP $\Longleftrightarrow$ DD $\Longleftrightarrow$ BCTP).



Scheme 36.

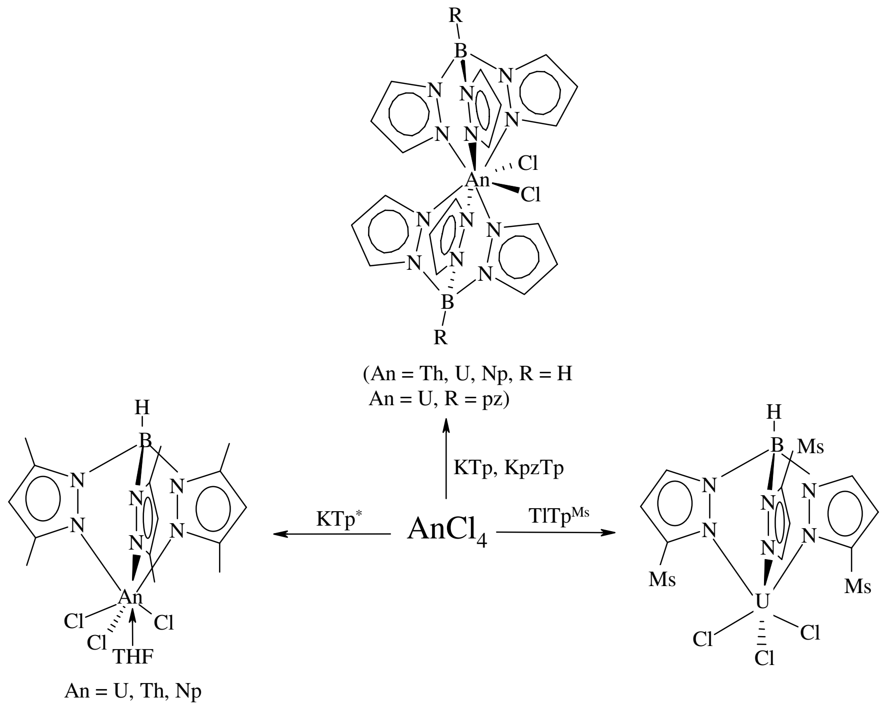
The replacement of one, two or three chlorides in [(κ^3-Tp*)AnCl$_3$(THF)] has also been possible, and a large number of alkoxide, amido, thiolate and alkyl derivatives were isolated and characterized The reactivity of some alkyl derivatives towards several unsaturated substrates was also evaluated [4,84,97]. This family of compounds can be six- or seven-coordinate, and presents a static behavior in solution [4,97].

Recently, Marques and coworkers [94] reported the complex [(κ^3-Tp$^{Ms^*}$)UCl$_3$], as well as some derivative chemistry (Scheme 38).

An interesting result was the characterization of the symmetrical complex [U(κ^3-Tp^{Ms})Cl$_3$] , which has been obtained during the recrystallization of an amido derivative. It has also been found that nitriles, isocyanides and acetone do not insert into the U–C bond of [(κ^3-TpMs*)U(C$_6$H$_4$CH$_2$NMe$_2$)Cl$_2$], but acetone reacts with this compound yielding the aldolate [(κ^3-TpMs*)U{η^2-(OC(Me)$_2$CH$_2$C(=O)Me}Cl$_2$] [94]. This reactivity is comparable to the one observed for the analogous [(κ^3-Tp*)UCl$_3$(THF)] [4]. Based on NMR results, the authors considered the Tp$^{Ms^*}$ a poorer electron donor than Tp*, and a less sterically demanding ligand. This last feature being due to the rearrangement of the Tp^{Ms} ligand during formation of the complex. The X-ray analysis of [(κ^3-Tp$^{Ms^*}$)UCl$_3$], [(κ^3-Tp^{Ms})UCl$_3$] and [(κ^3-Tp*)U{N(SiMe$_3$)$_2$}Cl$_2$] revealed that the uranium center has octahedral geometry with the ligand coordinating in its usual κ^3-mode [94].

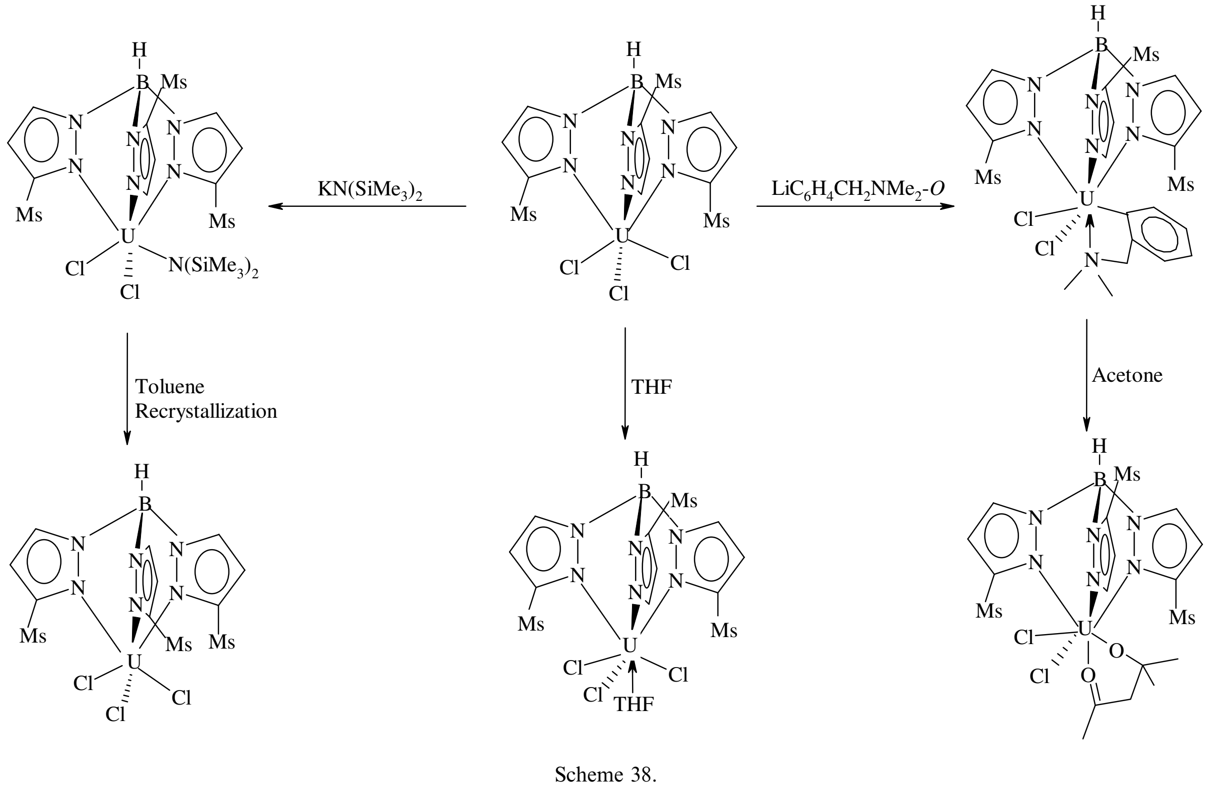
4. Final remarks

In the last few years a resurgence of interest in the chemistry of rhenium scorpionates is clear from the plethora of contributions and a variety of complexes, mainly anchored by Tp, pzTp and Tp* and with metal in the oxidation states +VII to +I, have been isolated. Using high valent oxides, several oxygen transfer reactions have been studied, allowing the stabilization of unusual neu-



Scheme 37.

tral and anionic Re(V) *trans*-dioxocomplexes anchored by pzTp or Bp′, and Re(VI) cationic *cis*-dioxocompounds anchored by Tp. Thermal and photochemical migration of alkyl or aryl groups from the metal to the oxo ligand have also been reported, for the first time. Catalytic oxygen transfer reactions have been studied using Re(V) oxides anchored by Tp* and pzTp, and a significant effect of the scorpionate ligand on these transfers was found.



Scheme 38.

A relatively *old compound*, a Re(I) dicarbonyl, has been reinvestigated and an impressive synthetic chemistry around it has been developed. Modulation of the electronic properties of the Re(I) metallic center allowed the stabilizing of rare monomeric η^2-aromatic compounds. A series of reactions involving selective transformation of the organic substrates has been described.

Among the actinides, uranium is still the most studied element and, in the last few years, its chemistry has been extended to the so called second generation of homo and heteroscorpionates. For U(III) it has been clearly shown that the type of compounds formed depends not only on the bulkiness but also on the symmetry of the 3-R substituents. The first mono-heteroscorpionate and bis-asymmetric heteroscorpionate complexes have been described and characterized, confirming the importance of modulating the steric profile of the ligand. This recently described U(III) chemistry certainly has opened a new avenue for heteroscorpionates as ancillary ligands.

5. Abbreviations

acac	acetylacetonate
An	actinides
BCTP	bicapped trigonal prismatic
bipy	bipyridine
Bp	dihydrobis(pyrazolyl)borate
Bp'	substituted dihydrobis(pyrazolyl)borate
Bp*	dihydrobis(3,5-dimethylpyrazolyl)borate
$Bp^{tBu,Me}$	dihydrobis(3-*tert*-butyl-5-methylpyrazolyl)borate
Bu	butyl (superscript n or *t* for normal or tertiary)
Cp*	pentamethylcyclopentadienyl
CpH	cyclopentadiene
DD	dodecahedral
dmpe	1,2-bis(dimethylphosphino)ethane
DMSO	dimethyl sulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
Et	ethyl
$Hpz^{tBu,Me}$	3-*tert*-butyl-5-methylpyrazole
Hpz^{Me_2}	3,5-dimethylpyrazole
8-hqnH	8-hydroxyquinoline
IR	infrared
Me	methyl
1-Meimz	1-methylimydazole
NAP	*N*-acetylpyrrole
NOE	nuclear overhauser effect
NMM	*N*-methylmaleimide
NMR	nuclear magnetic resonance
NTol	*p*-tolylimido
OTf	triflate, OSO_2CF_3
Ph	phenyl
Ph'	substituted pheny
Ph_2Bp	diphenylbis(pyrazolyl)borate
PhTp	phenyltris(pyrazolyl)borate
Pr	propyl (superscript *i* or *n* for iso or normal)
py	pyridine
py-O	pyridine *N*-oxide
pzH	pyrazole
$pz'H$	substituted pyrazole
pzTp	tetrakis(pyrazolyl)borate
R.T.	room temperature
SAP	square antiprismatic
2-S-py	pyridine-2-thiolate
THF	tetrahydrofuran
tim^{Me}	1-methyl-2-mercaptoimidazole
Tp	hydrotris(pyrazolyl)borate
Tp*	hydrotris(3,5-dimethylpyrazolyl)borate
Tp^{Ms}	hydrotris(3-mesitylpyrazolyl)borate
Tp^{Ms*}	hydrotris(5-mesitylpyrazolyl)borate

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References

[1] S. Trofimenko, Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, 1999.

[2] C.C. Romão, in: R.B. King (Ed.), Encyclopedia of Inorganic Chemistry, vol. 6, Wiley, New York, 1994, p. 3437.

[3] A. Paulo, J.D.G. Correia, I. Santos, Trends Inorg. Chem. 5 (1998) 57.

[4] I. Santos, N. Marques, New J. Chem. 19 (1995) 551.

[5] I.A. Degnan, W.A. Herrmann, E. Herdtweck, Chem. Ber. 123 (1990) 1347.

[6] B.J. Coe, Polyhedron 9 (1992) 1085.

[7] A. Domingos, J. Marçalo, A. Paulo, A. Pires de Matos, I. Santos, Inorg. Chem. 32 (1993) 5114.

[8] R. Garcia, Y.H. Xing, Â. Domingos, A. Paulo, I. Santos, Inorg. Chim. Acta 343 (2003) 27.

[9] J.E. Joachim, C. Apostolidis, B. Kanellakopulos, R. Maier, M.L. Ziegler, Z. Naturforsch. 48b (1993) 227.

[10] Y. Matano, T.O. Northcutt, J. Brugman, B.K. Bennet, S. Lovell, J.M. Mayer, Organometallics 19 (2000) 2781.

[11] M.J. Abrams, A. Davison, A.G. Jones, Inorg. Chim. Acta 82 (1984) 125.

[12] J.A. Thomas, A. Davison, Inorg. Chim. Acta 190 (1991) 231.

[13] A. Paulo, A. Domingos, J. Marçalo, A. Pires de Matos, I. Santos, Inorg. Chem. 34 (1995) 2113.

[14] A. Paulo, J. Marçalo, A. Pires de Matos, I. Santos, in: M. Nicolini, G. Bandoli, U. Mazzi (Eds.), Technetium and Rhenium in Chemistry and Nuclear Medicine, SGEditoriali, Padova, 1995, p. 227.

[15] K.P. Gable, A. Abubaker, K. Zientara, A.M. Wainwright, Organometallics 18 (1999) 173.

[16] K.P. Gable, E.C. Brown, Organometallics 19 (2000) 944.

[17] K.P. Gable, P. Chuawong, A.F.T. Yokochy, Organometallics 21 (2002) 929.

[18] H.A. Hinton, H. Chen, T.A. Hamor, F.S. McQuillan, C.J. Jones, Inorg. Chim. Acta 285 (1999) 55.

[19] I.A. Degnan, J. Behm, M.R. Cook, W.A. Herrmann, Inorg. Chem. 30 (1991) 2165.

[20] D.D. DuMez, T.O. Northcutt, Y. Matano, J.M. Mayer, Inorg. Chem. 38 (1999) 3309.

[21] S.N. Brown, Ph.D. Thesis, University of Washington, 1994.

[22] S.N. Brown, J.M. Mayer, J. Am. Chem. Soc. 116 (1994) 2219.

[23] D.D. DuMez, J.M. Mayer, Inorg. Chem. 37 (1998) 445.

[24] R.W. Thomas, G.W. Estes, R.C. Elder, E. Deutsch, J. Am. Chem. Soc. 101 (1979) 4581.

[25] G.B. Dahmann, J.H. Enemark, Inorg. Chem. 26 (1987) 3960.

[26] R.W. Thomas, A. Davison, H.S. Trop, E. Deutsch, Inorg. Chem. 19 (1980) 2840.

[27] A. Duatti, F. Tisato, F. Refosco, U. Mazzi, M. Nicolini, Inorg. Chem. 28 (1989) 4565.

[28] F. Tisato, C. Bolzati, A. Duatti, G. Bandoli, F. Refosco, Inorg. Chem. 32 (1993) 2042.

[29] A. Duatti, F. Tisato, F. Refosco, A. Moresco, U. Mazzi, G. Bandoli, M. Nicolini, in: M. Nicolini, G. Bandoli, U. Mazzi (Eds.), Technetium and Rhenium in Chemistry and Nuclear Medicine, SGEditoriali, Padova, 1989, p. 129.

[30] D. Nunes, A. Domingos, A. Paulo, L. Patrício, I. Santos, M.F.N.N. Carvalho, A.J.L. Pombeiro, Inorg. Chim. Acta 271 (1998) 65.

[31] D.D. DuMez, J.M. Mayer, Inorg. Chem. 34 (1995) 6396.

[32] S.N. Brown, J.M. Mayer, J. Am. Chem. Soc. 118 (1996) 12119.

[33] S.N. Brown, J.M. Mayer, Inorg. Chem. 31 (1992) 4091.

[34] A. Paulo, A. Domingos, A. Pires de Matos, I. Santos, M.F.N.N. Carvalho, A.J.L. Pombeiro, Inorg. Chem. 33 (1994) 4729.

[35] L.H. Doerrer, J.R. Galsworthy, M.L.H. Green, M.A. Leech, J. Chem. Soc., Dalton Trans. (1998) 2483.

[36] A. Paulo, A. Domingos, I. Santos, Inorg. Chem. 35 (1996) 1798.

[37] C.S. Masui, J.M. Mayer, Inorg. Chim. Acta 251 (1996) 325.

[38] J.W. Faller, A.R. Lavoie, Organometallics 19 (2000) 3957.

[39] P.B. Kettler, Y. Chang, Q. Chen, J. Zubieta, M.J. Abrams, S.K. Larsen, Inorg. Chim. Acta 231 (1995) 13.

[40] W.S. McNeil, D.D. DuMez, Y. Matano, S. Lovell, J.M. Mayer, Organometallics 18 (1999) 3715.

[41] B.K. Bennet, T.J. Crevier, D.D. DuMez, Y. Matano, W.S. McNeil, J.M. Mayer, J. Organomet. Chem. 591 (1999) 96.

[42] A. Paulo, Ph.D. Thesis, Instituto Superior Técnico, Technical University of Lisbon, 1998.

[43] A. Paulo, A. Domingos, I. Santos, J. Chem. Soc., Dalton Trans. (1999) 3735.

[44] D.D. DuMez, J.M. Mayer, J. Am. Chem. Soc. 118 (1996) 12416.

[45] A. Paulo, K.R. Reddy, A. Domingos, I. Santos, Inorg. Chem. 37 (1998) 6807.

[46] A. Paulo, A. Domingos, I. Santos, in: M. Nicolini, G. Bandoli, U. Mazzi (Eds.), Technetium and Rhenium in Chemistry and Nuclear Medicine, SGEditoriali, Padova, 1999, p. 245.

[47] K.R. Reddy, A.. Domingos, A. Paulo, I. Santos, Inorg. Chem. 38 (1999) 4278.

[48] A. Paulo, A. Domingos, R. Garcia, I. Santos, Inorg. Chem. 39 (2000) 5669.

[49] S.N. Brown, J.M. Mayer, Organometallics 14 (1995) 2951.

[50] S.H. Meiere, B.C. Brooks, T.B. Gunnoe, E.H. Carrig, M. Sabat, W.D. Harman, Organometallics 20 (2001) 3661.

[51] T.B. Gunnoe, S.H. Meiere, M. Sabat, W.D. Harman, Inorg. Chem. 39 (2000) 6127.

[52] S.N. Brown, J.M. Mayer, Inorg. Chem. 34 (1995) 3560.

[53] D.G. Hamilton, X.L. Luo, R.H. Crabtree, Inorg. Chem. 28 (1989) 3198.

[54] A. Paulo, J. Ascenso, A. Domingos, A. Galvão, I. Santos, J. Chem. Soc., Dalton Trans. (1999) 1293.

[55] Y. Matano, S.N. Brown, T.O. Northcutt, J.M. Mayer, Organometallics 17 (1998) 2939.

[56] S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 3904.

[57] S. Trofimenko, J. Am. Chem. Soc. 91 (1969) 588.

[58] J.A. McCleverty, I. Wolochowicz, J. Organomet. Chem. 169 (1979) 289.

[59] M. Angaroni, G.A. Ardizzoia, G. D'Alfonso, G. La Monica, J. Chem. Soc., Dalton Trans. (1990) 1895.

[60] J.E. Joachim, C. Apostolidis, B. Kanellakopulos, R. Maier, N. Marques, D. Meyer, J. Müller, A.P. Matos, B. Nuber, J. Rebizant, M.L. Ziegler, J. Organomet. Chem. 448 (1993) 119.

[61] A. Bond, M. Green, J. Chem. Soc. (A) (1971) 682.

[62] R. Garcia, A. Paulo, A. Domingos, I. Santos, K. Ortner, R. Alberto, J. Am. Chem. Soc. 122 (2000) 11240.

[63] A.R. Schoenberg, W.P. Anderson, Inorg. Chem. 11 (1972) 85.

[64] J.E. Joachim, C. Apostolidis, B. Kanellakopulos, D. Meyer, B. Nuber, K. Raptis, J. Rebizant, M.L. Ziegler, J. Organomet. Chem. 492 (1995) 199.

[65] R. Alberto, W.A. Herrmann, P. Kiprof, F. Baumgärtner, Inorg. Chem. 31 (1992) 895.

[66] J.E. Joachim, C. Apostolidis, B. Kanellakopulos, R. Mayer, D. Meyer, J. Rebizant, M.L. Ziegler, J. Organomet. Chem. 455 (1993) 137.

[67] T.B. Gunnoe, M. Sabat, W.D. Harman, J. Am. Chem. Soc. 120 (1998) 8747.

[68] T.B. Gunnoe, M. Sabat, W.D. Harman, J. Am. Chem. Soc. 121 (1999) 6499.

[69] T.B. Gunnoe, M. Sabat, W.D. Harman, Organometallics 19 (2000) 728.

[70] S.H. Meiere, B.C. Brooks, T.B. Gunnoe, M. Sabat, W.D. Harman, Organometallics 20 (2001) 1038.

[71] L.A. Friedman, S.H. Meiere, B.C. Brooks, W.D. Harman, Organometallics 20 (2001) 1699.

[72] S.H. Meiere, W.D. Harman, Organometallics 20 (2001) 3876.

[73] S.H. Meiere, F. Ding, L.A. Friedman, M. Sabat, W.D. Harman, J. Am. Chem. Soc. 124 (2002) 13506.

[74] B.C. Brooks, S.H. Meiere, L.A. Friedman, E.H. Carrig, T.B. Gunnoe, W.D. Harman, J. Am. Chem. Soc. 123 (2001) 3541.

[75] S.H. Meiere, M.T. Valahovic, W.D. Harman, J. Am. Chem. Soc. 124 (2002) 15099.

[76] M.D. Chordia, P.L. Smith, S.H. Meiere, M. Sabat, W.D. Harman, J. Am. Chem. Soc. 123 (2001) 10756.

[77] L.A. Friedman, M. Sabat, W.D. Harman, J. Am. Chem. Soc. 124 (2002) 7395.

[78] L.A. Friedman, W.D. Harman, J. Am. Chem. Soc. 123 (2001) 8967.

[79] M.T. Valahovic, T.B. Gunnoe, M. Sabat, W.D. Harman, J. Am. Chem. Soc. 124 (2002) 3309.

[80] C. Apostolidis, A. Carvalho, A. Domingos, B. Kanellakopulos, R. Maier, N. Marques, A. Pires De Matos, J. Rebizant, Polyhedron 18 (1–2) (1999) 263.

[81] R. McDonald, Y.M. Sun, J. Takats, V.W. Day, T.A. Eberspracher, J. Alloys Compd. 213/214 (1994) 8.

[82] Y.M. Sun, R. McDonald, J. Takats, V.W. Day, T.A. Eberspracher, Inorg. Chem. 33 (1994) 4433.

[83] I. Santos, N. Marques, A. Pires de Matos, J. Less-Common Met. 122 (1986) 215.

[84] A. Domingos, N. Marques, A. Pires de Matos, I. Santos, M. Silva, Organometallics 13 (1994) 654.

[85] Sun Y. Ph.D. Thesis, University of Alberta, 1995.

[86] A.J. Amoroso, J.C. Jeffery, P.L. Jones, J.A. Mccleeverty, L. Rees, A.L. Rheingold, Y.M. Sun, J. Takats, S. Trofimenko, M.D. Ward, G.P.A. Yap, J. Chem. Soc., Chem. Commun. (1995) 1881.

[87] (a) L. Maria, A. Domingos, I. Santos, Inorg. Chem. Commun. 6 (1) (2003) 58;
(b) L. Maria, A. Domingos, I. Santos, Personal communication at ICCC XXXVth International Conference on Coordination chemistry, Heidelberg, 2002;
(c) L. Maria, PhD Thesis, IST, Lisbon, 2003.
[88] Y.M. Sun, J. Takats, W.T. Eberspracher, V. Day, Inorg. Chim. Acta 229 (1-2) (1995) 315.
[89] A. Carvalho, A. Domingos, P. Gaspar, N. Marques, A. Pires de Matos, I. Santos, Polyhedron 11/12 (1992) 1481.
[90] L. Maria, M.P.C. Campello, A. Domingos, I. Santos, R. Andersen, J. Chem. Soc., Dalton Trans. 12 (1999) 2015.
[91] L. Maria, A. Domingos, I. Santos, Inorg. Chem. 42 (2003) 3323.
[92] A. Domingos, M.R.J. Elsegood, A.C. Hiller, G. Lin, S.Y. Liu, I. Lopes, N. Marques, G.H. Maunder, R. McDonald, A. Sella, J.W. Steed, J. Takats, Inorg. Chem. 41 (2002) 6761.
[93] M.P.C. Campello, A. Galvão, A. Domingos, A.P. De Matos, I. Santos, J. Organomet. Chem. 579 (1999) 5.
[94] M. Silva, A. Domingos, A.P. De Matos, N. Marques, S. Trofimemko, J. Chem. Soc., Dalton Trans. 24 (2000) 4628.
[95] M.P.C. Campello, M.J. Calhorda, A. Domingos, A. Galvão, J.P. Leal, A.P. De Matos, I. Santos, J. Organomet. Chem. 538 (1-2) (1997) 223.
[96] M.P.C. Campello, Ph.D. Thesis, FCL, Lisboa, 1998.
[97] M. Silva, N. Marques, A.P. De Matos, J. Organomet. Chem. 493 (1995) 129.