

Review

# Rhenium and technetium complexes with N-heterocyclic carbenes – A review

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## Abstract

The coordination chemistry of technetium and rhenium with N-heterocyclic carbenes of the dimethylimidazol-2-ylidene and 1,2,4-triazol-5-ylidene types is reviewed. Compounds containing the metals in the oxidation states “+7”, “+5” and “+1” are introduced. General trends and differences in the chemical behaviour of the complexes, particularly between the different metal cores (oxo, nitrido, imido) of Tc(V) and Re(V) compounds, are discussed. The influence of electronic and steric factors for the stabilisation of the metal complexes is explored.

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*Keywords:* Rhenium; Technetium; Carbene complexes; N-Heterocyclic carbene; Review

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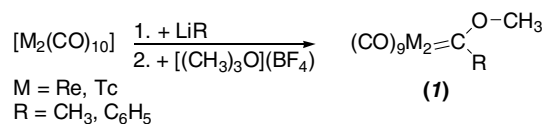
## 1. Introduction

Despite the fact that carbene complexes of rhenium and technetium have been known for quite a long time,

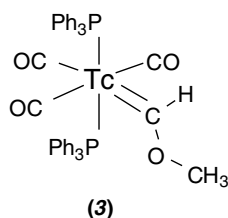
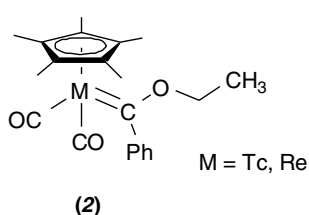
the chemistry of Re and Tc complexes with N-heterocyclic carbenes (NHCs) is surprisingly poorly explored. The first crystallographically characterised representatives were not published until 2003 [1,2]. This lack of knowledge is unexpected considering the extensive coordination chemistry of such ligand systems with almost all transition metals [3] and the wide range of applications that representatives of this group of compounds have found in various fields [4].

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The first carbene complexes of technetium and rhenium, which were isolated in 1972, belong to the classical 'Fischer-type'. They were prepared by the addition of LiCH<sub>3</sub> or LiC<sub>6</sub>H<sub>5</sub> to [Tc<sub>2</sub>(CO)<sub>10</sub>] or [Re<sub>2</sub>(CO)<sub>10</sub>] and subsequent methylation. The products have the general formula [(CO)<sub>9</sub>M<sub>2</sub>C(OCH<sub>3</sub>)R] (**1**) (M = Re, Tc; R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) [5], and this synthetic route has successfully been applied for further examples containing additional {Cp\*}<sup>-</sup> (**2**) or PPh<sub>3</sub> ligands (**3**) [6,7].

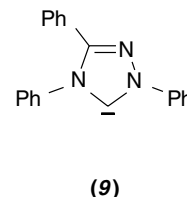
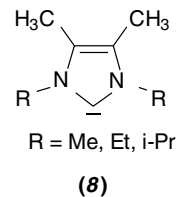
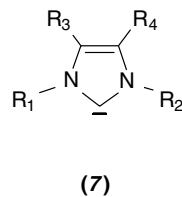


Cationic diaminocarbene complexes of the composition [Re(CO)<sub>5</sub>{C(NHPh)NHR}]<sup>+</sup> (**4**) were prepared by the reaction of [Re(CO)<sub>5</sub>]<sup>-</sup> with unsymmetrical carbodiimides PhN=C=NR (R = Pr<sup>i</sup>, Bu<sup>t</sup>) and subsequent protonation [8]. Similar products, the neutral [ReBr(CO)<sub>4</sub>{C(NHPh)NHR}] complexes (R = Pr<sup>i</sup>, Pr), are formed when the isocyanide complex [ReBr(CO)<sub>4</sub>(CNPh)] is treated with propylamine or isopropylamine [9]. They react with Et<sub>2</sub>NH to yield the cyclometalated products [Re(CO)<sub>4</sub>{η<sup>2</sup>-C(NHR)(NHC<sub>6</sub>H<sub>4</sub>)}] (**5**) (R = Pr<sup>i</sup>, Pr) [10]. The reactivity of the Re–C σ-bonds of the cyclometalated diaminocarbene complexes was demonstrated by the facile electrophilic addition of HBr, RCO<sub>2</sub>H, or I<sub>2</sub> at room temperature, and it could be exploited to prepare a series of rhenium diaminocarbene derivatives. Prolonged heating of the nitrile derivatives [ReBr(CO)<sub>3</sub>(CNPh)(NCMe)] with excess amine yields the diaminocarbene complexes [ReBr(CO)<sub>3</sub>(NH<sub>2</sub>R)-{C(NHPh)-(NHR)}] and [Re(CO)<sub>3</sub>(NH<sub>2</sub>R)<sub>2</sub>{C(NHPh)-

(NHR)}]Br [11]. Similar products were obtained by a photochemical reaction of [Re<sub>2</sub>(CO)<sub>10</sub>] with tetramethylthiourea, which led to the cleavage of the S=C bond and the formation of two pentanuclear compounds of the composition [Re<sub>5</sub>(CO)<sub>17</sub>(μ-R)(μ<sub>4</sub>-S){C(NMe<sub>2</sub>)<sub>2</sub>}<sub>2</sub>] (R = SH or OH) [12].

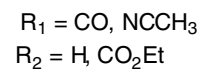
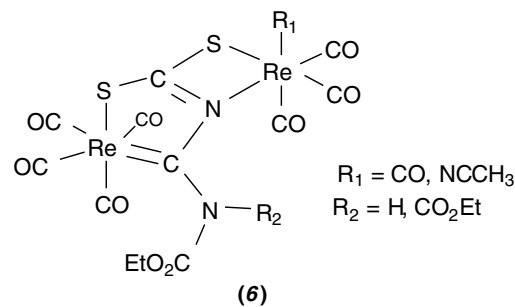
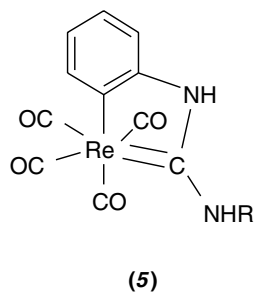
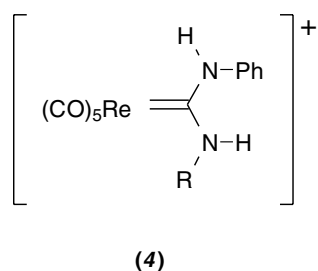
The insertion of the organic isothiocyanate EtO<sub>2</sub>CN=C=S into the rhenium–rhenium single bond of [Re<sub>2</sub>(CO)<sub>9</sub>(MeCN)] and subsequent rearrangement results in the formation of two dimeric compounds (**6**), which each contain one (EtO<sub>2</sub>C)<sub>2</sub>NC=NCS<sub>2</sub> ligand [13,14]. The central unit of this moiety can formally be regarded as a heteroatom-stabilised carbene functionality.

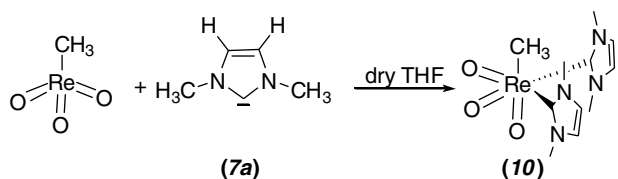
Today, many different types and subtypes of NHCs are known [3], but in this review, which comprises the chemistry of technetium and rhenium, we can restrict our discussion to two basic types which are derived from imidazole (**7** and **8**) and 1,3,4-triphenyl-1,2,4-triazol-5-ylidene (**9**). The carbenes of type **7** are commonly obtained by deprotonation of the corresponding imidazolium salts by strong bases or a metal hydride [15–18], while the 4,5-dimethylimidazol-2-ylidenes of type **8** are readily available by the reduction of corresponding imidazol-2(3*H*)-thiones with potassium in boiling THF [19]. The stable triazole derivative **9** is obtained by the thermal elimination of methanol from 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazole [20].



## 2. Re(VII) and Re(VI) complexes

Reports of N-heterocyclic carbene complexes focus mainly on compounds containing transition metals in low oxidation states. Only a few reports are available which refer to carbene complexes containing transition metals in high oxidation states.





Treatment of  $[\text{CH}_3\text{ReO}_3]$  with methyl derivative **7a** in dry THF gives  $[\text{CH}_3\text{ReO}_3(\mathbf{7a})_2]$  (**10**) [21]. The yellow powder thus obtained was studied spectroscopically, but proved to be unstable above  $-20^\circ\text{C}$  and could not be characterised by X-ray crystallography. Elemental analysis, IR and NMR data, however, give evidence for a hexacoordinate bis(carbene) complex **10**. The  $^{13}\text{C}$  NMR signal of the carbene carbon atom is found at  $\delta = 176.7$  ppm ( $\text{CD}_3\text{CN}$ ), which is comparable to the chemical shift in other carbene complexes.

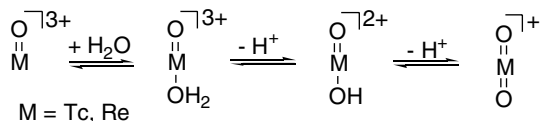
$\text{Re}_2\text{O}_7$  reacts with **7a** under reduction of the metal and the formation of a violet Re(VI) complex [21]. The insoluble compound has not yet been structurally characterised, but the concomitant formation of Re(VI) has been confirmed by cyclic voltammetry [22].

### 3. Re(V) and Tc(V) compounds

By far, the largest number of structurally characterised rhenium and technetium complexes contain the metal in the oxidation state “+5” [23,24]. This can be attributed to the high stability of the rhenium(V) and technetium(V) oxo, nitrido, and imido cores with a great variety of ligand systems. The dominance of  $\text{O}^{2-}$ ,  $\text{N}^{3-}$ , and  $\text{NR}^{2-}$  ligands can be rationalized by the fact that they are excellent  $\pi$ -donors and, therefore, stabilise high oxidation states.

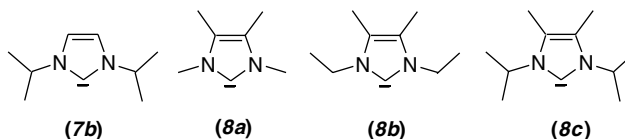
#### 3.1. Oxo complexes

The oxo core has multiple manifestations, with mono- and dioxo- as well as  $\mu$ -oxo bridged species being common. They are related to each other by the addition (and subsequent deprotonation) of water ligands in the sixth position of square-pyramidal monooxometal(V) complexes. Subsequently, the  $[\text{MO}]^{3+}$ ,  $[\text{MO}(\text{OH}_2)]^{3+}$ ,  $[\text{MO}(\text{OH})]^{2+}$ , and  $[\text{MO}_2]^+$  cores ( $\text{M} = \text{Tc}, \text{Re}$ ) can be formed (Scheme 1). Particularly the aqua and hydroxo ligands *trans* to the monooxo ligand are subject to ongoing exchange reactions with solvent molecules or other monodentate ligands depending on the composition of the reaction mixture. The relative stability of the cores



Scheme 1.

depends on the ligands present, with anionic ligands favouring the monooxo core and neutral ones tending to form dioxo species. This trend is also observed with NHC ligands of the types **7** or **8**, which prefer the stable dioxo core when four of them occupy the equatorial coordination sphere of the complex. Depending on the steric bulk of the ligands, there are also examples of monooxo complexes with  $\text{Cl}^-$  or  $\text{CH}_3\text{O}^-$  co-ligands.



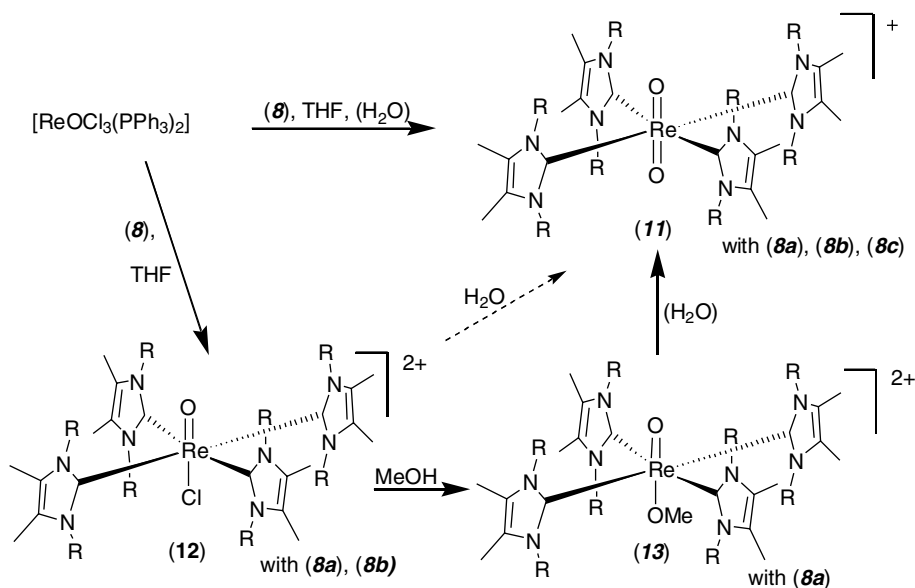
The first Re(V) and Tc(V) dioxo NHC complexes with **8c** were published in 2003 [1]. Irrespective of the rhenium and technetium starting materials (various mono and dioxo compounds, as well as nitrido complexes)  $[\text{MO}_2(\mathbf{8c})_4]^+$  cations (**11**) ( $\text{M} = \text{Tc}, \text{Re}$ ) were formed. A more detailed study with 1,3-dialkyl substituted 4,5-dimethylimidazol-2-ylidenes (**8a–8c**) showed that the composition and the stability of the products are controlled by the alkyl substituents of the nitrogen atoms of the organometallic ligands [25].

Reactions of **8** with  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  under atmospheric conditions yield various mono- and dioxorhenium(V) complexes. They all contain four of the NHC ligands bonded equatorially in a paddle-wheel-like arrangement (see Scheme 2) [25].

With an excess of **8a**,  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  can be converted to  $[\text{ReOCl}(\mathbf{8a})_4]\text{Cl}_2$  (**12a**), which precipitates from the reaction solution as a green powder. Dissolution of this solid in methanol leads to the exchange of the chloro ligand for a methoxo ligand, which is accompanied by a colour change to dark red. After the addition of  $(\text{NH}_4)(\text{PF}_6)$ , deep red crystals of  $[\text{ReO}(\text{OCH}_3)(\mathbf{8a})_4](\text{PF}_6)_2$  (**13a**) are isolated. Traces of water in the solvent lead to formation of  $[\text{ReO}_2(\mathbf{8a})_4](\text{ReO}_4)$  as a side product. Both in solution and in the solid state,  $[\text{ReO}(\text{OCH}_3)(\mathbf{8a})_4](\text{PF}_6)_2$  is stable to air and water for a limited amount of time.

When the analogous reaction is performed with **8b**, a similar result is observed. A green precipitate can be isolated from the brown reaction mixture. Upon dissolution in methanol, no colour change is observed, and addition of  $\text{K}(\text{PF}_6)$  yields green crystals containing the complex cation  $[\text{ReOCl}(\mathbf{8b})_4]^{2+}$  (**12b**).

When an excess of **8c** is treated with various rhenium(V) oxo complexes such as  $[\text{ReOCl}_3(\text{PPh}_3)_2]$ ,  $(\text{NBu}_4)[\text{ReOCl}_4]$ , or  $[\text{Re}_2\text{O}_3\text{Cl}_4(\text{py})_4]$  under ambient conditions, there is no evidence for the formation of the intermediate complex  $[\text{ReOCl}(\mathbf{8c})_4]^{2+}$ , and only the dioxo cation  $[\text{ReO}_2(\mathbf{8c})_4]^+$  (**11c**) is recovered. Orange-red blocks of the cation as its perrhenate salt can be recovered upon standing at room temperature. Addition of  $(\text{NH}_4)(\text{PF}_6)$  yields  $[\text{ReO}_2(\mathbf{8c})_4](\text{PF}_6)$  as orange-red



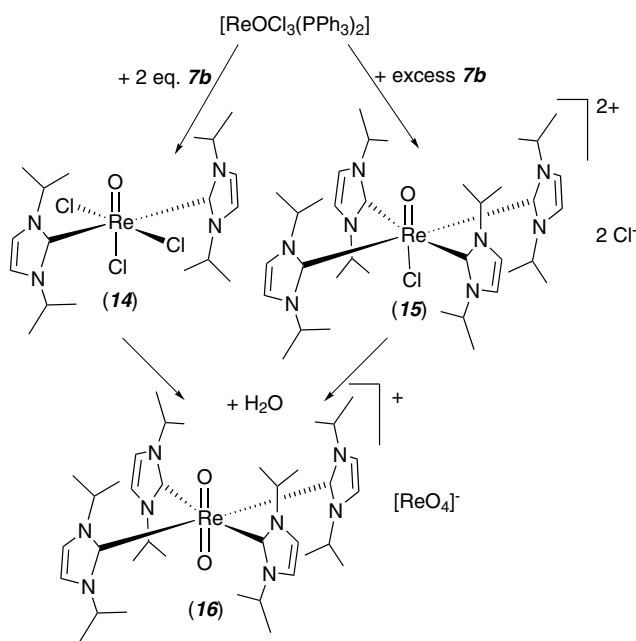
Scheme 2.

blocks. These salts are stable indefinitely in solution and as solids.

This different reactivity of the ligands is apparently an effect of the appreciable steric bulk of the isopropyl groups and indicates that the difference in steric hindrance between the isopropyl and ethyl substituents plays a decisive role in the structure of such NHC complexes. Furthermore, calculations show that the basicity of the ligands increases in the series  $\text{R} = \text{Me} < \text{R} = \text{Et}$  (not calculated)  $< \text{R} = i\text{-Pr}$  [26]. This means that the *iso*-propyl derivative has a more nucleophilic carbene carbon atom and thus donates more electron density to the metal centre. This increased electron density can be better stabilised by a dioxo core.

Reactions at low temperatures allow the isolation of ligand exchange intermediates with ligand **7b** [2].  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  reacts with 2 equiv. of **7b** at  $-20^\circ\text{C}$  under formation of  $[\text{ReOCl}_3(\text{7b})_2]$  (**14**), which was isolated as a green crystalline solid. With an excess of (**7b**)  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  reacts at  $-20^\circ\text{C}$  to the green dicationic complex  $[\text{ReOCl}(\text{7b})_4]\text{Cl}_2$  (**15**). As solids, neither compound shows decomposition when exposed to air for short periods of time, but in solution the compounds are moisture-sensitive. Traces of water lead to formation of  $[\text{ReO}_2(\text{7b})_4][\text{ReO}_4]$  (**16**). The  $[\text{ReO}_2(\text{7b})_4]^+$  cation was also obtained by reaction of  $[\text{ReO}_2\text{I}(\text{PPh}_3)_2]$  and  $[\text{ReO}_2\text{-Me}(\text{PhCCPh})]$  with an excess of the NHC ligand [2] (see Scheme 3).

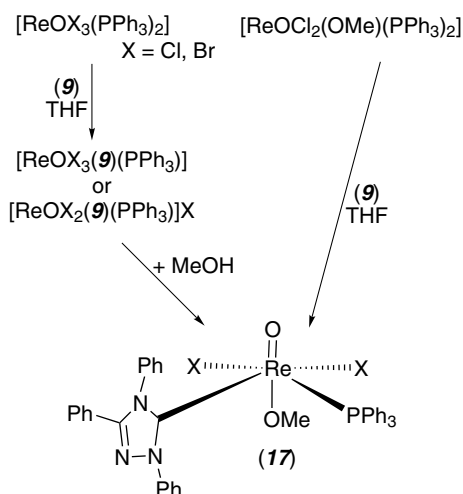
The first technetium complex with an NHC ligand,  $[\text{TcO}_2(\text{8c})_4][\text{TcO}_4]$ , was prepared from  $(\text{NBu}_4)[\text{TcOCl}_4]$  and an excess of **8c** at room temperature. The yellow crystals of the pertechnetate salt are stable in dry air. The X-ray crystal structure shows that the structure of the complex cation is similar to that of  $[\text{ReO}_2(\text{8c})_4]^+$  [1].



Scheme 3.

The metal atoms in all complexes with four carbene ligands are effectively shielded by the four equatorial carbene ligands. This may explain the remarkable stability of these complexes and the fact that high oxidation states of the transition metals are effectively stabilised.

1,3,4-Triphenyl-1,2,4-triazol-5-ylidene (**9**) is less nucleophilic than the imidazol-2-ylidene carbenes. For this reason, reactions proceed slower and under thermodynamic control. When solutions of  $[\text{ReOX}_3(\text{PPh}_3)_2]$



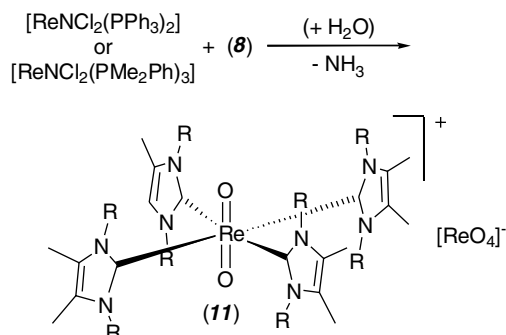
Scheme 4.

(X = Cl, Br) are treated with **9**, a dusky pink microcrystalline solid is formed, which is most probably  $[\text{ReOX}_3(\mathbf{9})(\text{PPh}_3)]$  or  $[\text{ReOX}_2(\mathbf{9})(\text{PPh}_3)]\text{X}$ . Recrystallization of the solid from methanol leads to  $[\text{ReOX}_2(\text{OMe})(\text{PPh}_3)(\mathbf{9})]$  (**17**) as dusky pink crystals (Scheme 4) [27]. A reaction starting from  $[\text{ReOBr}_2(\text{OMe})(\text{PPh}_3)_2]$  yields (**17**) directly from the THF mother liquor. An interesting structural feature of **17** is the *cis* position of the two bulky ligands. The compounds are stable indefinitely in solution and as solids. Ligand exchange products with more than one triazol-5-ylidene have not yet been isolated, in contrast to the situation with corresponding nitridorhenium(V) complexes.

### 3.2. Nitrido complexes

The 1,3-dialkyl-4,5-dimethylimidazol-2-ylidene ligands (**8**) possess a high nucleophilic power at the carbene carbon atom, which enables the ligands to activate nitridorhenium(V) complexes. Reaction of **8**

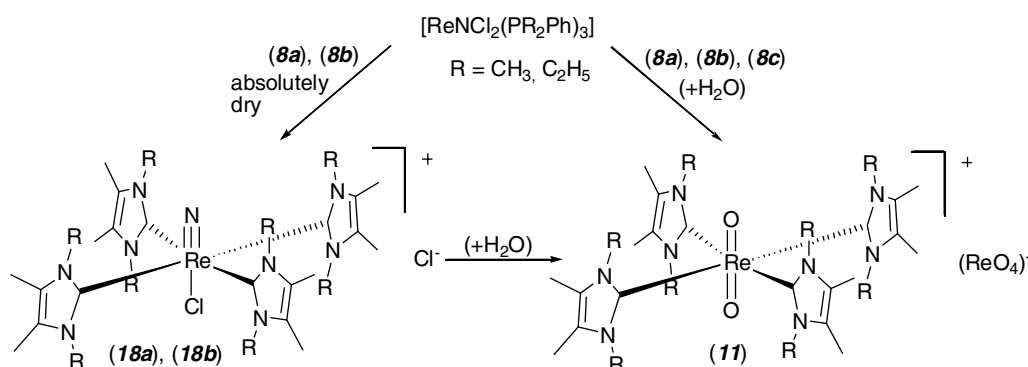
with the common nitridorhenium(V) precursors  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  or  $[\text{ReN}(\text{PMe}_2\text{Ph})_3\text{Cl}_2]$  in THF on air lead to cleavage of the rhenium–nitrogen triple bond and to the formation of  $[\text{ReO}_2(\mathbf{8})_4][\text{ReO}_4]$  (**11**) under release of  $\text{NH}_3$ .



This behaviour is very unusual for rhenium, and there are only a handful of examples where rhenium– or technetium–nitrogen triple bonds are cleaved under mild conditions [23,24]. Under absolute exclusion of moisture (and oxygen), however, it is possible to isolate nitridorhenium complexes with the methyl and ethyl derivatives **8a** and **8b**, while this has not yet been successful with the isopropyl substituted ligand **8c** [28].

$[\text{ReNCl}(\mathbf{8b})_4]\text{Cl}$  (**18b**) is formed by treatment of  $[\text{ReN}(\text{PMe}_2\text{Ph})_3\text{Cl}_2]$  or  $[\text{ReN}(\text{PEt}_2\text{Ph})_3\text{Cl}_2]$  with an excess of **8b** in dry THF or benzene (Scheme 5). After isolation from the mother liquor, the orange-red crystals are surprisingly stable in air and in cold MeOH solutions. Decomposition and the formation of  $[\text{ReO}_2(\mathbf{8b})_4][\text{ReO}_4]$  is observed in boiling MeOH.

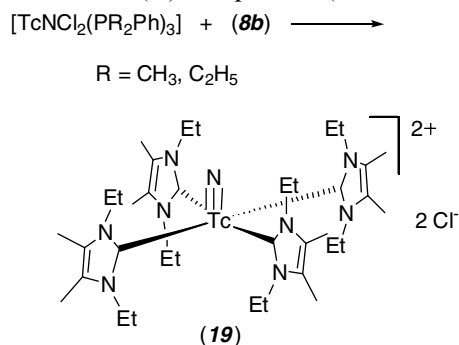
$[\text{ReNCl}(\mathbf{8a})_4]\text{Cl}$  (**18a**) can be obtained following the same procedure. The yellow powder is stable in air, but unlike  $[\text{ReNCl}(\mathbf{8b})_4]\text{Cl}$ , it rapidly decomposes in solution. This difference is apparently an effect of the less shielded metal centre due to the smaller steric bulk of the methyl substituted ligand. The obvious differences between the coordination properties of the ligands of type



Scheme 5.

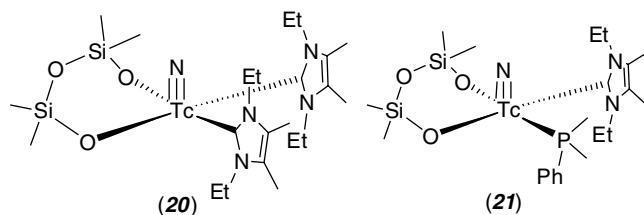


**8** and the stability of the resulting nitridorhenium complexes is similar to the results which have been observed for the oxorhenium(V) compounds (cf. Section 3.1).



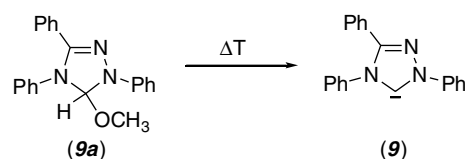
Stable nitridotechnetium(V) complexes with NHC ligands were prepared from  $[\text{TcNCl}_2(\text{PR}_2\text{Ph})_3]$  complexes (R = Me, Et) and **(8b)** when the reaction is performed under complete exclusion of air and moisture [29],  $[\text{TcN}(\mathbf{8b})_4]\text{Cl}_2$  (**19**) precipitates from the reaction mixture as a yellow powder and can be recrystallized from  $\text{CH}_3\text{NO}_2$ . The product is stable in air as a solid; solutions, however, slowly decompose and an increasing amount of the hydrochloride of the ligand can be detected with increasing time in the NMR spectra of solutions of the complex. The coordination sphere of the five-coordinate technetium atom is a square pyramid. This is a remarkable difference to the six-coordinate rhenium atom in the analogous complex  $[\text{ReNCl}(\mathbf{8b})_4]\text{Cl}$  (**18b**) [28].

As side products of the reactions of  $[\text{TcNCl}_2(\text{PMe}_2\text{Ph})_3]$  or  $[\text{TcNCl}_2(\text{PET}_2\text{Ph})_3]$  with **(8b)**, two complexes with 1,1,3,3-tetramethyldisiloxane-1,3-diolato ligands,  $[\text{TcN}(\mathbf{8b})_2(\text{OSiMe}_2\text{OSiMe}_2\text{O})]$  (**20**) and  $[\text{TcN}(\mathbf{8b})(\text{PMe}_2\text{Ph})(\text{OSiMe}_2\text{OSiMe}_2\text{O})]$  (**21**), were isolated. The silicon-containing ligands are the result of serendipitous activation of silicon grease by the highly nucleophilic carbene [29].



The strong nucleophilic character of the NHCs of type **8** is also reflected by another accidental reaction, the formation of a tetranuclear compound of the composition  $[\{\text{ReN}(\text{PMe}_2\text{Ph})_3\}_2(\text{ReO}_3\text{N})_2]$  during the interaction of  $[\text{ReNCl}_2(\text{PMe}_2\text{Ph})_3]$  with **(8b)** [30]. Although the carbene is not a constituent of the product, it initiates the formation of the  $\{\text{ReN}(\text{PMe}_2\text{Ph})_3\}^{2+}$  fragment and the  $[\text{ReO}_3\text{N}]^{2-}$  anion by the abstraction of ligands from the metal. Similar reactions have also been observed with other strong bases [30].

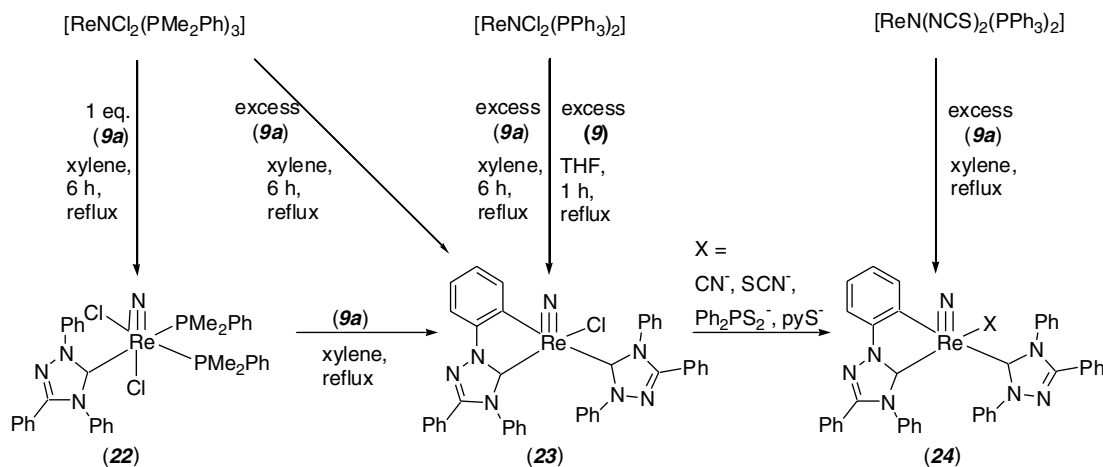
The stable carbene 1,3,4-triphenyl-1,2,4-triazol-5-ylidene (**9**) can readily be prepared by thermal decomposition of 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol (**9a**) under vacuum. MeOH is abstracted during this procedure and **9** is obtained as a pure compound in nearly quantitative yield [20]. This general route can be applied directly for the synthesis of new carbene complexes with **9**, provided that the educt and product compounds possess a sufficient thermal stability, since the decomposition of **9a** requires temperatures  $>80^\circ\text{C}$ . Stable NHC nitridorhenium(V) complexes can be obtained by reactions of **9a** or the isolated carbene 1,3,4-triphenyl-1,2,4-triazol-5-ylidene (**9**) with the nitridorhenium(V) precursors  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  or  $[\text{ReNCl}_2(\text{PMe}_2\text{Ph})_3]$  [31,32].



The orange-yellow  $[\text{ReNCl}_2(\text{PMe}_2\text{Ph})_2(\mathbf{9})]$  (**22**) is obtained in a one-pot synthesis from equivalent amounts of  $[\text{ReNCl}_2(\text{PMe}_2\text{Ph})_3]$  and **9a** in boiling xylene (Scheme 6). The carbene ligand is formed in situ upon heating of the triazol and can be used without prior isolation. The product is an air stable solid which does not decompose at ambient temperatures as a solid or in solution.

Prolonged heating of  $[\text{ReNCl}_2(\text{PMe}_2\text{Ph})_3]$  with an excess of **9a** results in the coordination of a second carbene ligand and orthometallation. The product,  $[\text{ReNCl}(\mathbf{9-H})(\mathbf{9})]$  (**23**), precipitates as a purple powder directly from the reaction mixture and forms deep red crystals upon crystallization from THF. It is the exclusive product when  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  is used as a rhenium precursor. The main reason for the orthometallation is most probably the steric bulk of **9**, which directs an ortho proton of one of the phenyl rings in a position that is relatively close to the metal atom. This orientation is also observed for the second (monodentate) carbene ligand, for which weak agostic interactions with Re were discussed [32]. Orthometallation is obviously not a direct consequence of the high reaction temperature, which is required for the in situ generation of **9**. This has been proven by the reaction of  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  with isolated (**9**), which can be performed under milder conditions such as short heating in boiling THF. The deep purple-red  $[\text{ReNCl}(\mathbf{9-H})(\mathbf{9})]$  (**23**) is stable as a solid and in solution and does not decompose even in the presence of moisture.

While the NHC ligands in complex **23** are inert, the chloro ligand is labile and subject to exchange reactions. This has been demonstrated by reactions with  $\text{KSCN}$ ,  $\text{KCN}$ , 2-mercaptopyridine and diphenyldithiophosphinic acid and the formation of products of the composi-



Scheme 6.

tion (**24**) [32]. In the case of the isothiocyanato complex  $[\text{ReN}(\text{NCS})(\text{9-H})(\text{9})]$ , the same product is obtained by a ligand exchange reaction starting from the isothiocyanate compound  $[\text{ReN}(\text{NCS})_2(\text{PPh}_3)_2]$  and an excess of **9a** in xylene.

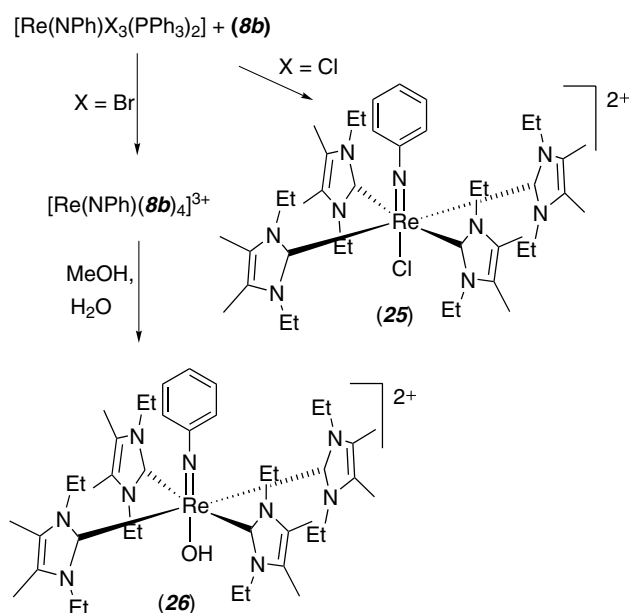
### 3.3. Imido complexes

The formally dianionic imido ligand “ $\text{NR}^{2-}$ ” is iso-electronic with the oxo ligand and also stabilises metals in their high oxidation states. Treatment of the imido-rhenium(V) compounds  $[\text{Re}(\text{NPh})\text{X}_3(\text{PPh}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with **8b** gave the first imidorhenium complexes with NHC ligands (Scheme 7).

The use of  $[\text{Re}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2]$  results in the formation of  $[\text{Re}(\text{NPh})\text{Cl}(\text{8b})_4]\text{Cl}_2$  (**25**) [28]. This compound precipitates as a green powder from THF. Dissolution

of the powder in MeOH, which is saturated with  $(\text{NH}_4)(\text{PF}_6)$ , yields  $[\text{Re}(\text{NPh})(\text{Cl})(\text{8b})_4](\text{PF}_6)_2$  as green crystals. The compound is stable as a solid and in solution. The chloro ligand in this complex is not subject to exchange reactions. An X-ray structure analysis shows that the chloro ligand is well shielded by the bulky carbene ligands and the space at the coordination site *trans* to the imido group is restricted.

This is confirmed by the experimental results of an attempted reaction of the analogous bromo derivative  $[\text{Re}(\text{NPh})\text{Br}_3(\text{PPh}_3)_2]$  with **8b**. Addition of **8b** to the bromo derivative in THF results in the immediate precipitation of a violet powder, which is most probably  $[\text{Re}(\text{NPh})(\text{8b})_4]\text{Br}_3$ . All attempts to obtain single crystals of this highly charged rhenium complex with a five-coordinate metal atom have failed up to now. Dissolution in wet methanol and subsequent addition of  $(\text{NH}_4)(\text{PF}_6)$  results in the formation of violet crystals of  $[\text{Re}(\text{NPh})(\text{OH})(\text{8b})_4](\text{PF}_6)_2$  (**26**) [28]. The coordination of a hydroxo ligand rather than a methoxo or bromo ligand can be understood by the limited space that is provided in the position *trans* to the phenylimido unit by an effective steric shielding due to the four carbene ligands. Similar experimental results have been obtained previously for oxo compounds, where a corresponding methanolato complex could be obtained exclusively for the methyl derivative **8a**, but not for the more bulky **8b** and **8c**.

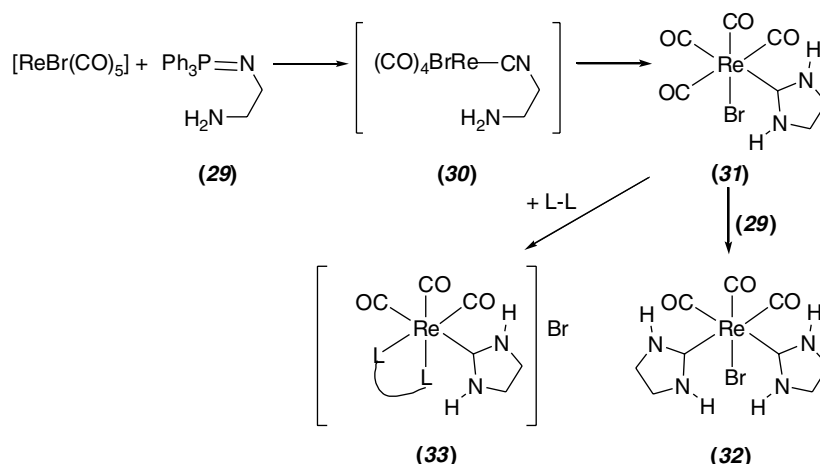


Scheme 7.

## 4. Rhenium(I) compounds

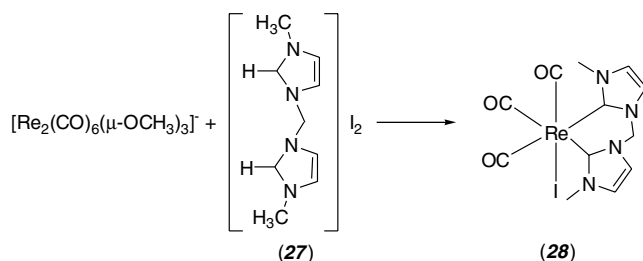
N-Heterocyclic carbene complexes are formally single Fischer-type carbenes. Accordingly, one focus of this research is directed towards compounds containing transition metals in low formal oxidation states. Surprisingly, there are only a few examples of NHC rhenium(I) complexes.

In 1992, Hermann et al. [33] showed that the complex  $[\text{N}(\text{CH}_3)_4][\text{Re}_2(\text{CO})_6(\mu\text{-OCH}_3)_3]$  acts as a good



Scheme 8.

surrogate for  $[\text{Re}_2(\text{CO})_{10}]$  and can be used for ready synthesis of complexes containing a  $\text{Re}(\text{CO})_3$  fragment. Accordingly, treatment of  $[\text{N}(\text{CH}_3)_4][\text{Re}_2(\text{CO})_6(\mu\text{-OCH}_3)_3]$  with the bis(imidazolium)iodide 1,1'-methylene-bis(3-methyl-1*H*-imidazolium)-diiodide (27) yields the bis(carbene)rhenium(I) complex  $[\text{Re}(\text{CO})_3(\text{27})]$  (28). The deprotonation of the bis(imidazolium)iodide occurs during this reaction without the addition of a supporting base.



Based on the work of Lu et al. [9], a different approach for the preparation of rhenium(I) NHC complexes was published in 1996. The nucleophilic attack of the aminophosphineimine  $\text{NH}_2(\text{CH}_2)_2\text{N}=\text{PPh}_3$  (29) at a carbonyl ligand of  $[\text{ReBr}(\text{CO})_5]$  gives an isocyanide complex 30 (Scheme 8), which undergoes a subsequent intramolecular cyclization under formation of the stable carbene complex 31 [34]. This compound is able to react with another equivalent of the aminophosphineimine under conversion of a second carbonyl ligand to give the corresponding bromotricarbonylbis(carbene)rhenium(I) complex 32. Complex 31 reacts with bidentate ligands (L–L) such as diimines or chelating phosphines under formation of cationic  $[\text{Re}(\text{CO})_3(\text{L-L})(\text{carbene})]^+$  complexes (33). The products possess interesting luminescent properties [35].

## 5. Conclusions

Although the coordination chemistry of rhenium and technetium with NHC ligands is relatively poorly devel-

oped, some recent work exists on such complexes with the metals in high oxidation states, which include compounds with remarkable stability. This stability is attributed to the large steric bulk of the ligands that provide an effective shielding of the metal centre. The new  $\text{Re}(\text{V})$  and  $\text{Tc}(\text{V})$  compounds contain the oxo, nitrido and imido cores and are the subject of further studies, which also include potential medical applications in cancer therapy and diagnostic and therapeutic nuclear medicine.

Some new rhenium(I) tricarbonyl NHC complexes possess promising luminescent properties and make such compounds interesting for further research.

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