New Organometallic Technetium Complexes in High and Low Oxidation States

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Summary

Synthesis and characterization of the first organometallic Tc(VII) complex CH_3TcO_3 is described. It behaves differently to CH_3ReO_3 concerning reactions with alkenes and with aromatic amine bases. Furthermore we present the synthesis and structure of the first organometallic cluster of Tc(I) $Na[Tc_3(CO)_9(\mu_3\text{-}OCH_3)(\mu_2\text{-}OCH_3)_3]$ with a cuban-like structure. The cluster act as a crown ether with high stability towards sodium. In the crystal the different cluster units are linked via an isocarbonyl bond. The cluster proved to be a useful educt for subsequent substitution reactions with tridentate ligands. Carbonylation of $TBA[TcO_4]$ under 1 atm CO finally gave in quantitative yield, the very versatile educt mer-$TcCl(CO)_3[P(C_6H_5)_3]_2$ which readily undergoes substitutions with several tridentate ligands.

Introduction

Over the last ten years organometallic complexes of rhenium and technetium have received considerable interest. Compounds of Re(VII) have proven to possess very interesting catalytic properties as well as acting as reactive precursors to a wide variety of organometallic complexes in lower oxidation states [1, 2]. The chemistry of the two rhenium compounds CH_3ReO_3 **1** and Cp*ReO_3 have received special interest among the few known Re(VII) compounds containing the "ReO_3" core which is isolobal to CH_3^+. In view of this, compound **1** was particularly intensively investigated concerning its catalytic properties [3]. Organometallic Tc(VII) complexes were previously not known and so we focused our attention on CH_3TcO_3 **2**, its properties, and when present, its catalytic reactivity. Only a very few Tc(VII) compounds containing the "TcO_3^+" are known (Figure 1) and with the exception of **3** all were prepared within the last three years [4, 5, 6, 7]. Synthesis of **5** and **6** goes along with the Re analog. We investigated the different behaviour of rhenium and technetium following example of CH_3TcO_3 with respect to oxidation catalysis and found the differences are not only gradual but fundamental.

As for the oxidation state +VII relatively little chemistry has been done for the +I state [8]. Since Tc-chemistry was often provoked by a possible application in radiodiagnostics Tc(I) seemed not to be very interesting, owing to the fact that this state typically belongs to the field of organometallic chemistry. This opinion was dramatically contradicted by the easy synthesis of Davisons $[Tc(CNR)_6]^+$ [9] or more recently by Westers $[Tc(C_6H_6)_2]^+$ [10]. A second reason is the difficulty in synthesizing homoleptic Tc-carbonyls, the most useful and common starting material for the development of low valency Tc-complexes. Literature routes end up with often poor yield [11, 12] and safety reasons are a hinderance to high pressure reactions with radioactive material. By lowering CO-pressure we were able to synthesize selectively and in high yield a reactive Tc(I)-cluster. It is obvious from reaction conditions that this cluster system is readily formed as an intermediate during the reduction step. Its interesting structure and subsequent reactions are presented. Further investigations with rhenium at different CO-pressures resulted in similar clusters with the difference that the reactions occured very much faster in the technetium case.

Synthesis, characterization and catalytic properties of CH_3TcO_3

Original synthesis of CH_3ReO_3 was straight forward and resulted in a 50% yield of the compound [13]. Reaction conditions were relatively severe, refluxing the solution in THF for 5—6 h. Under the same conditions we were not able to isolate the desired Tc-product as can be seen from Figure 2.

Instead, a 50% yield of the trimethylstannylester **4** was isolated as well as around 40% (relative to Tc) of the dimeric Tc(VI) compound **7**. This orange product is easily sublimable, soluble in all kinds of organic solvents and stable in air. Its structure has been determined (Figure 3) [14]. It is well possible that compound **2** is formed as an intermediate but that it is readily reduced further to the Tc(VI) compound **7**. With strong reducing agents such as $Zn(CH_3)_2$ the analog Re complex can be synthesized. The fact that the stannyl ester is formed as well supports this as-
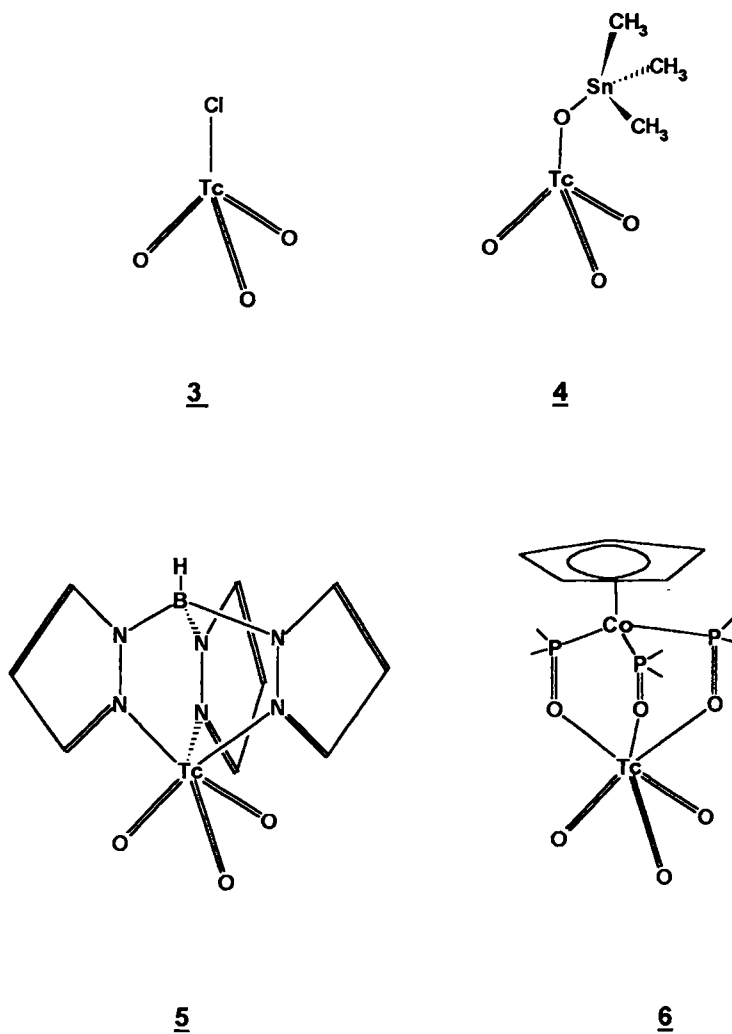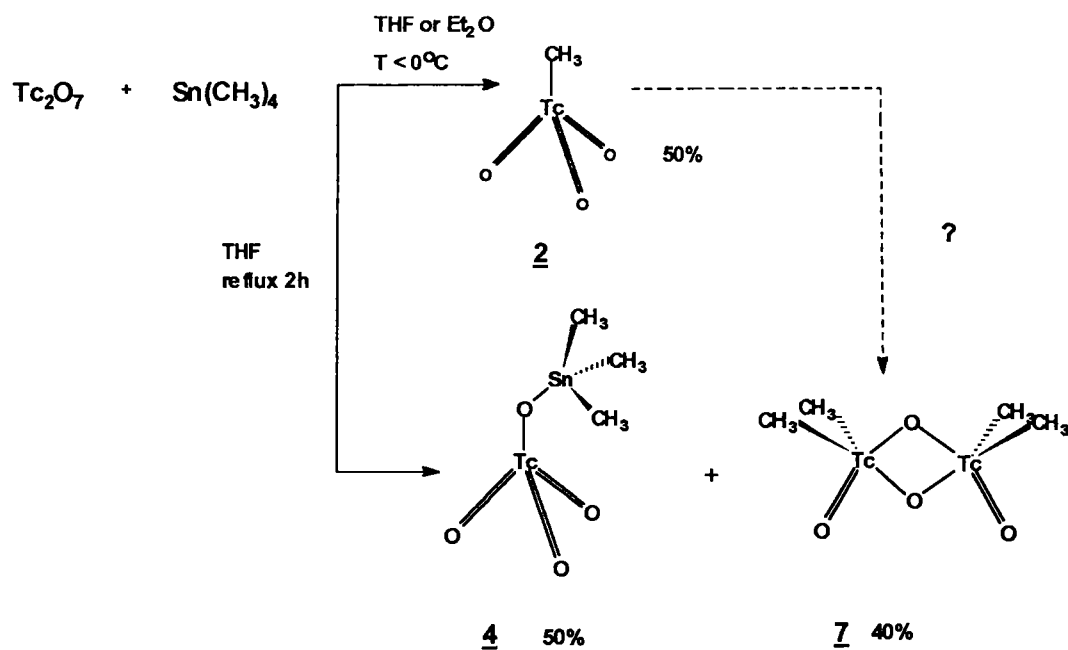
Fig. 1. Some Tc(VII) complexes containing the "TcO₃" core.

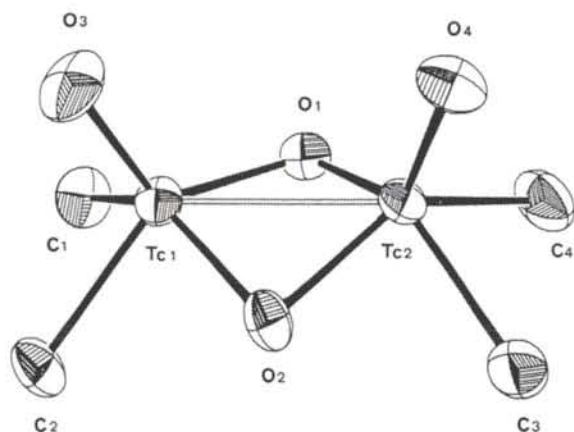Fig. 2. Reaction conditions for the synthesis of compound 2, 4 and 7.

Fig. 3. ORTEP drawing of the complex $[(CH_3)_4Tc_2O_4]$. Thermal ellipsoids are at the 50% probability level.

sumption. The course of the reaction indicates also that the difference in redox potential influences the chemistry significantly. The structure of compound **7** is isomorphous to that of rhenium. The Tc−Tc distance of 256.17(3) pm could give rise to a Tc−Tc single bond. Extreme line broadening in ^1H and ^{99}Tc-NMR suggests the compound to be paramagnetic, thus contradicting the assumption of a Tc−Tc single bond.

The synthesis of CH_3TcO_3 was finally done at low temperature, at best below $-20\,^\circ$C. Running the reaction at $0\,^\circ$C the solution slowly turned orange but nevertheless CH_3TcO_3 could be isolated. This coloring of the solution obviously resulted from formation of small amounts of compound **7**.

CH_3TcO_3 is an extremely volatile compound that can be sublimed at room temperature and atmospheric pressure. It forms long white needles if sublimed at $-78\,^\circ$C. It is stable at room temperature and decomposes on hot parts only forming probably TcO_3 and C_2H_6. It is soluble in all solvents including water. Stock solutions were usually prepared in hexane at low temperature. It has been characterized by ^{1}H-NMR, ^{99}Tc-NMR, MS and IR-spectroscopy. An important difference to its rhenium analog is the fact that no phenanthroline or bipyridile adduct could be precipitated. This can be done with CH_3ReO_3 to stabilize the coordinatively unsaturated CH_3ReO_3 unit [15]. On adding one of these bases intense red solutions were obtained, which decomposed on concentrating. The assumption that this behaviour could be due to high C−H acidity i.e. that we have a kind of acid/base equilibrium, is interesting but could not be proven.

Catalytic reactions

It is well established that CH_3ReO_3 acts as a powerful epoxidation catalyst of alkenes. Subsequent hydrolyzation ends up with either trans-diolates (alkaline) or mixture of cis/trans-diolates (acidic). When a solution of CH_3TcO_3 was mixed with stoichiometric amounts of an alkene an intense yellow color formed immediately. On addition of water a black precipitate formed readily and TcO_4^- could be detected chromatographically. Tc(V) compounds are known to undergo easy disproportion to Tc(IV) and Tc(VII). The assumption that compound **8** (Figure 4) is formed can therefore be proven indirectly. GC/MS investigations of the remaining solution allowed the detection of diols. We especially used cyclohexene as a model to investigate stereochemistry. Derivatization of the diols with trimethylsilylchloride allowed us to differ between the trans and the cis isomere on a special GC column. We found that the cis-isomer was formed specifically. The mechanism of reduction and formation of the intermediate **8** which could not be isolated seemed to be similar to that with OsO_4 described by Sharpless *et al.* [16]. If the reaction is carried out in the presence of water free H_2O_2 in tert.-BuOH this process occurs also catalytically (Figure 4). In the case of cyclohexene the yield of cis-1,2-cyclohexanediol was 83% for a ratio catalyst/alkene $= 1:100$. Presence of small amounts of water interrupt the catalytic cycle by hydrolyzing the reduced form of the catalyst. It could be observed that black precipitates formed as the reaction went on.

Davison *et al.* used $TcClO_3$phen for a similar purpose [17]. On reacting this compound with alkene (e.g. ethene) a stable Tc(V) complex was formed by reduction. It was not tried to run the cycle catalytically but since this compound is coordinatively saturated it is unlikely that the process runs under mild conditions. For the analog Re(VII) complex [$ReClO_3$phen] a completely different behaviour was found in that this compound did not add alkenes but the otherwise prepared [$ReOCl(phen)(OCH_2CH_2O)$] released alkenes on heating to form [$ReClO_3$phen].

The differences between Re(VII) and Tc(VII) reveal that chemistry in this oxidation state is not only gradual but fundamentally different. Figure 5 gives an excerpt of the periodical table. Manganese and ruthenium are related to each other in that there highest oxides cleave carbon carbon double bonds and the alkenes end up as carbonyls. Technetium and osmium on the other hand react smoother and oxidize stereospecifically to cis-diolates (derivatives). Rhenium at least is able to epoxidize alkenes in the presence of peroxides.

New Tc(I) and Re(I) compounds

Another aspect of our recent work on organometallic technetium complexes was to find an easy access to reactive Tc(I) compounds. The usual approach is the complete carbonylation of Tc_2O_7 or TcO_2 under high pressure and temperature to form the long known $Tc_2(CO)_{10}$ as starting material [18, 19]. Yields are moderate and the procedure, especially in the case of
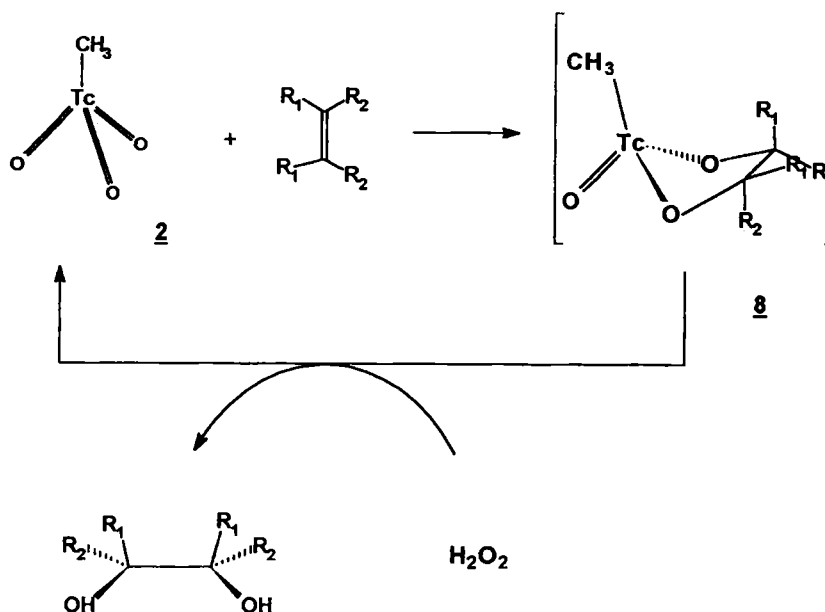
Fig. 4. Catalytic cycle for the oxidation of alkenes using CH_3TcO_3 as catalyst.
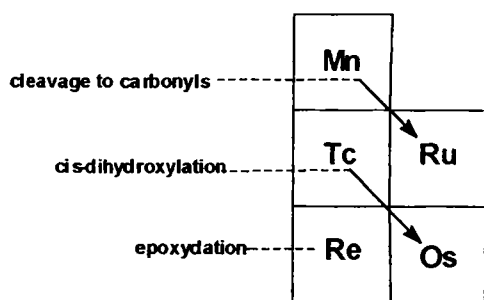

Fig. 5. Excerpt of the periodical system showing relations of oxidativ behaviour against alkenes.

sensitive Tc_2O_7, is complicated. Investigation of the formation of possible intermediates formed during this seven electron reduction step has not been done for the group 7a and scarcely for other elements. Preferable, in the presence of a potential coordinating solvents it is to be expected that stable intermediates are formed. We intended to prepare selectively such intermediates by control of pressure, temperature and reaction time. We used $NaTcO_4$ as starting material and CH_3OH as solvent for the above mentioned reasons. Heinekey *et al.* described a procedure to prepare $Re_2(CO)_{10}$ in high yield [20]. Figure 6 gives an overview on our reaction conditions.

Heinekeys protocol could also be reproduced with technetium resulting in high yield access to $Tc_2(CO)_{10}$. Varying thermodynamic conditions such as pressure, temperature and time we isolated in good yield the cluster-like intermediate $Na[Tc_3(CO)_9(\mu_3\text{-}OCH_3)(\mu_2\text{-}OCH_3)_3]$ 9. It is formed in over 75% yield after only 2 h of reaction time at conditions which are moderate compared to a total carbonylation. 9 can subsequently be further reduced to $Tc_2(CO)_{10}$ by applying the original conditions. It seems that the reduction to $Tc(I)$

goes very quickly while the further one electron reduction step is very slow. It is to be expected that $Na[Tc_3(CO)_9(\mu_3\text{-}OCH_3)(\mu_2\text{-}OCH_3)_3]$ is not the only intermediate formed but it may be in the technetium case the only one that is present in high steady state concentrations [21]. This described cluster 9 is the first trinuclear $Tc(I)\text{-}CO$ cluster. Its structure could be elucidated and revealed some special features. A "Schakal" presentation is given in Figure 7.

Even though there are only three Tc-atoms the basic frame is that of a cube. The sodium atom included in the formula does not just act as a counterion but is strongly included in the cluster system. Neither in acetonitrile, ethanol nor in a water/acetonitrile mixture could any conductivity be measured. Therefore the moiety $[Tc_3(CO)_9(\mu_3\text{-}OCH_3)(\mu_2\text{-}OCH_3)_3]^-$ can be described as an anionic crown ether with high stability toward sodium. Another interesting speciality is the detection of isocarbonyl bonding between a sodium atom from one cluster and a CO from a neighbouring unit, forming thus indefinitely long cluster chains linked by Tc-C-O-Na. The sodium is further coordinated by two CH_3CN molecules and uses one CO to saturate its coordination sphere. Only a few isocarbonyl complexes are known [22]. The bond length of 251.0(5) pm lies at the upper range of determined C-O--Na distances.

The described $Na[Tc_3(CO)_9(\mu_3\text{-}OCH_3)(\mu_2\text{-}OCH_3)_3]$ is not only an interesting structure but a very versatile educt for subsequent $Tc(I)$ chemistry. The coordinated methanolato groups are strongly labilized by trans effect of carbonyls and are thus easily substituted. Figure 8 gives some examples of such reactions which can all be performed in good yields. Again ^{99}Tc-NMR of the three complexes has been done. It shows that 11 and 12 fall inside the range proposed for $Tc(I)$
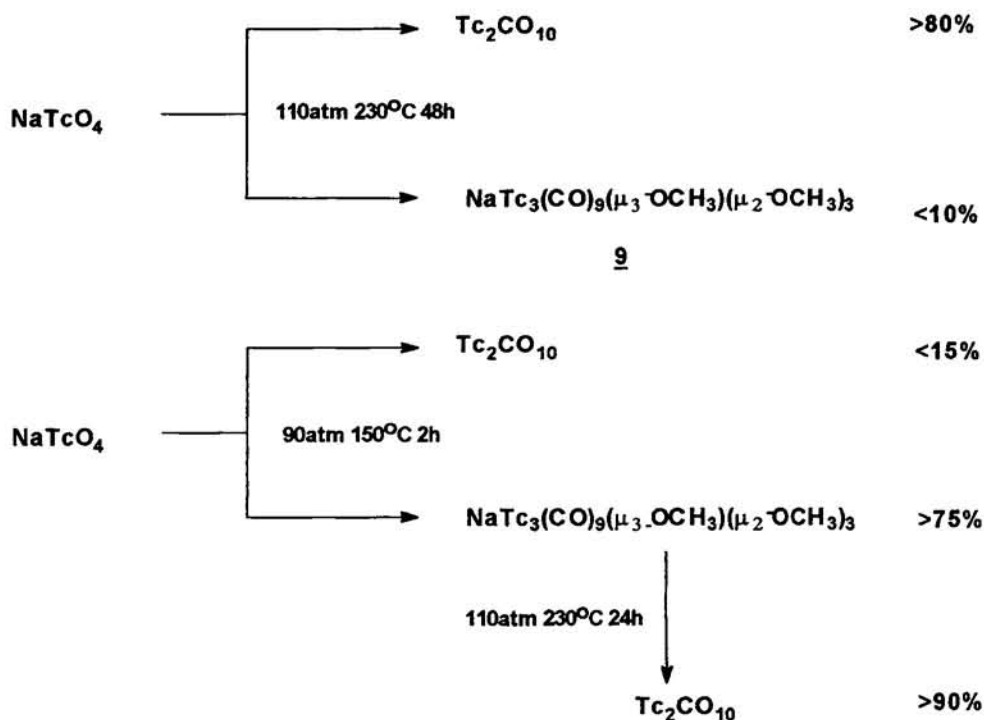
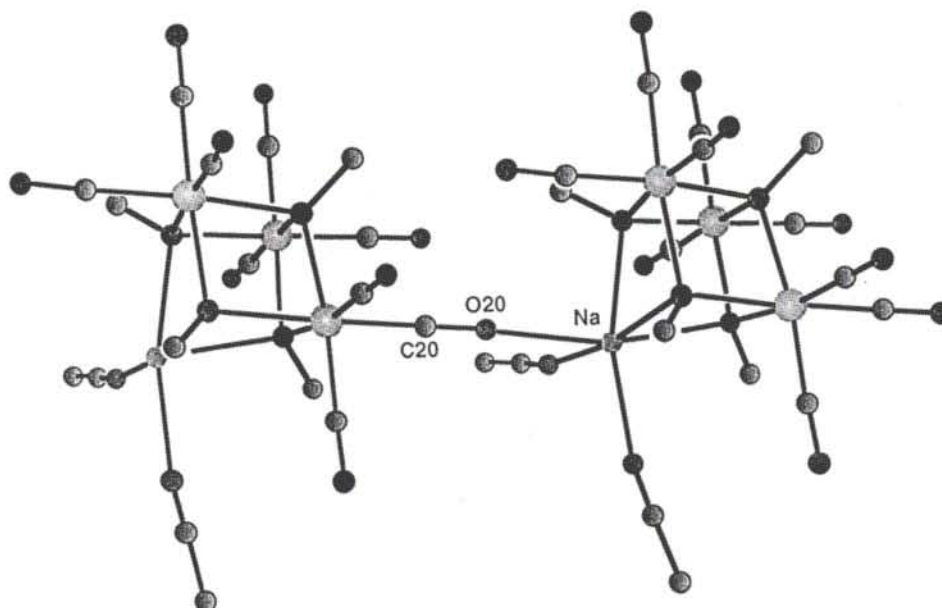Fig. 6. Carbonylation of $NaTcO_4$: product distribution under different conditions.

Fig. 7. "Schakal" presentation of two $[NaTc_3(CO)_9(OCH_3)_4]$ units linked by the isocarbonyl bond "O20 − Na".

complexes while **10** resonates rather far outside this range [23].

Investigation on Re(I)-clusters

To compare rhenium and technetium similar carbonylations have been done with perrhenate. Figure 9 gives the results. Again, at high pressure and temperature $Re_2(CO)_{10}$ was obtained in high yield. At decreased pressure but same temperature and time, a dinuclear Re(I) complex $[(CO)_3Re(\mu_2\text{-}OCH_3)_3\text{-}Re(CO)_3]^-$ **13** was found in almost quantitative yield [24]. Another decrease in pressure by 50% leaving time and temperature almost the same gave in 60% yield the same trinuclear Re(I)-cluster $[Re_3(CO)_9(\mu_3\text{-}OCH_3)(\mu_2\text{-}OCH_3)_3]^-$ **14** as in the technetium cases. A further decrease in pressure down to 20 atm yielded low amounts of a tetranuclear cluster. Elemental analysis as well as mass spectroscopy indicates a μ_3-oxo included into the structure. Investigations on this matter are to be pursued.
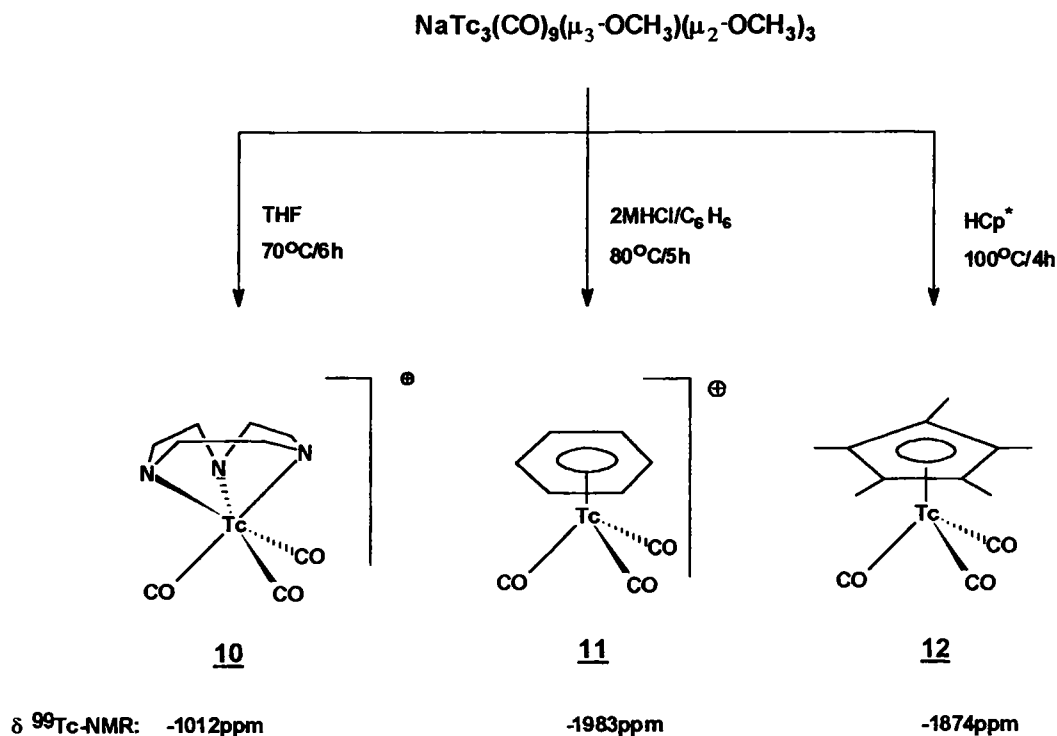
$$NaTc_3(CO)_9(\mu_3\text{-}OCH_3)(\mu_2\text{-}OCH_3)_3$$

Fig. 8. Substitution reactions on [NaTc₃(CO)₉(OCH₃)₄] using tridentate facial coordinating ligands.

It seems that during the reduction process of perrhenate a lot of (extractable) intermediates are formed. They can be selectively obtained through pressure and temperature control. The conditions to yield, for example, the trinuclear unit [Re₃(CO)₉(μ₃-OCH₃)(μ₂-OCH₃)₃]⁻ are much stronger than in the technetium case. This mirrors again the often observed effect that technetium reacts much more readily than rhenium and that the former is easier to reduce than the latter. To achieve the same yield of as in the case of 9, reaction times have to be twenty times as long as for 9. To prove that solubilities are not responsible for the observed delayed kinetic the same reactions were done using NaReO₄. Under similar conditions similar yields and species were obtained.

The structure of the not yet described dimeric compound 13 was resolved. It consists of two facial "Re(CO)₃" moieties linked by three bridging methanolato groups. The Re — Re distance is 311.3 pm and a single bond can therefore be excluded.

Oxidation of Cp*Tc(CO)₃

The oxidation of Cp*Re(CO)₃ was originally done with a two layer system consisting of benzene and H₂O₂/H₂SO₄ in moderate yield. We developed a much faster and higher yield synthesis of Cp*ReO₃ by using Mn₂O₇ in acetone or CCl₄ as oxidizing agent [25]. This powerful oxidant is able to transform Cp*Re(CO)₃ in minutes to the desired product. In the technetium case we hoped to apply the same method. Oxidation with H₂O₂ to Cp*TcO₃ failed and we could not even isolate the polymer [Cp*Tc₂O₃]ₙ described by Kanellakopu-

los and coworkers [26]. The attempt to oxidize with Mn₂O₇ failed as well and the observation was made that some reactive intermediate or the educt technetium compound catalytically decomposed Mn₂O₇. Adding one drop of a Cp*Tc(CO)₃ solution to Mn₂O₇ in CCl₄ at −78°C induced readily the evolution of a gas (O₂) and the formation of bulky MnO₂ was observed. Using other oxidants such as dimethyl-dioxirane as described by Wolowiec et al. [27] we found no Cp*TcO₃ but recovered the educt quantitatively.

Synthesis and reactions of complexes containing the "mer-Tc(I)(CO)₂P(C₆H₅)₃" moiety

Beside the not readily available "fac-Tc(CO)₃" unit it seems to be easier to get to the meridional coordination geometry of three molecules of CO. In 1977 Mazzi and coworkers described a route to mer-TcCl(CO)₃[P(C₆H₅)₃]₂ using the Tc(IV)-educt TcCl₄(P(C₆H₅)₃)₂ under one atmosphere of CO [28]. The choice of an educt with an odd number of electrons seemed not very convenient since reduction goes with two electron steps thus ending either with Tc(0) or Tc(II). We therefore chose well known [TcOCl₄]⁻ as our educt. In an easy synthesis the very useful mer-TcCl(CO)₃[P(C₆H₅)₃]₂ 16 could be prepared in quantitative yield (Figure 10) [29].

It is important that the first reduction step is done with an oxophilic species such as P(C₆H₅)₃. In a one pot synthesis starting with TBA[TcO₄] and a two layer system the same compound was found. Trop [30] described in 1979 the synthesis of the compound 17 which obviously could be an intermediate in our pro-
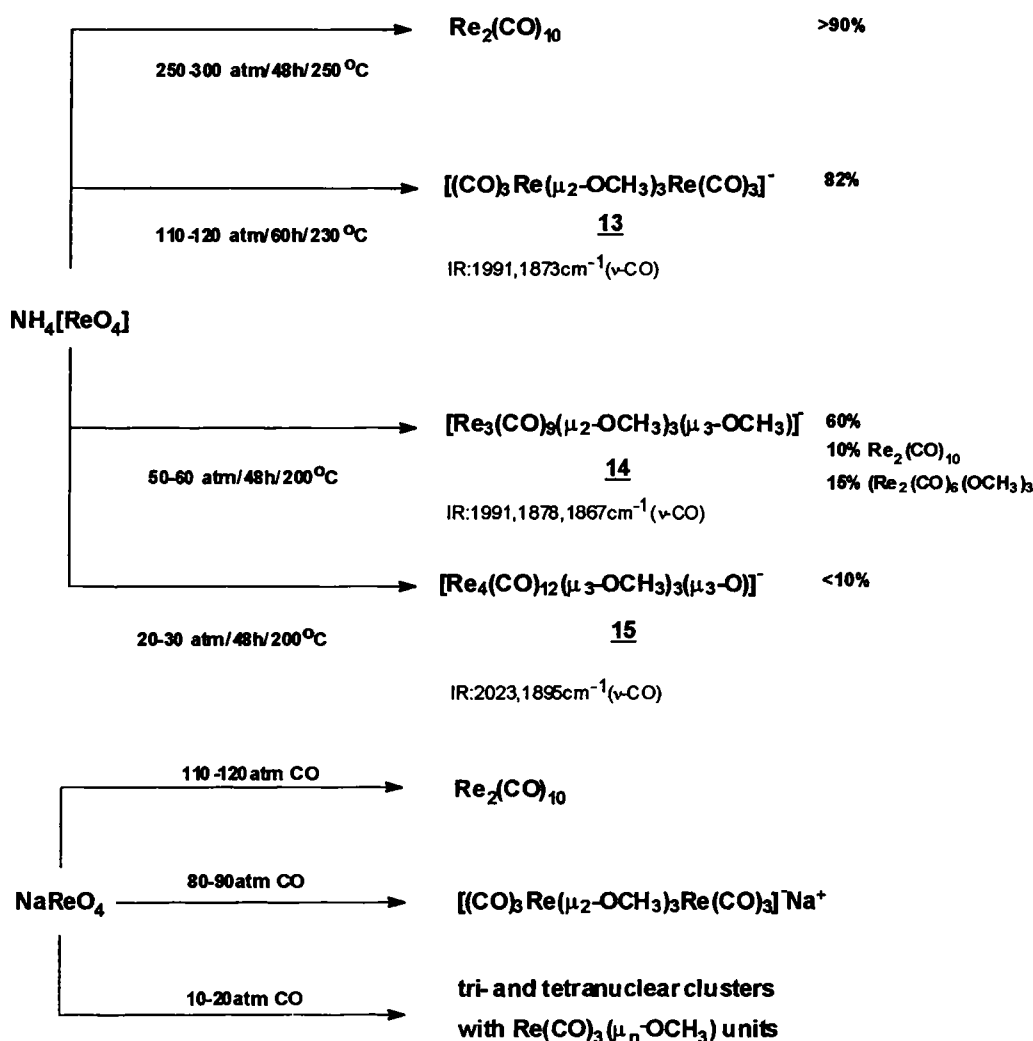
Fig. 9. Carbonylation of NH4[ReO4]: product distribution under different conditions.

tocol. **17** is orange and insoluble in toluene. Pearlstein *et al.* found in 1989 [31] that the acetonitrile ligand is substituted by small π-accepting molecules such as CO to form deep red complex **18** which also could be expected to be an intermediate in our synthesis. Neither one of these species was observed and if ever they are only present in very low steady state concentrations. The X-ray structure of compound **16** was resolved. The two phosphines are trans to each other and the three carbonyls are in a meridional coordination geometry.

Substitution reactions on mer-TcCl(CO)₃[P(C₆H₅)₃]₂

We focused special interest again on facial coordinating tridentate amines and [C₅Me₅]⁻. As shown in Figure 11 substitution occured easily and in good yield. The main products were compounds of the general formula [LTc(CO)₂P(C₆H₅)₃]. IR-spectroscopy of the raw product let us assume that also some small amounts of [LTc(CO)₃] had been formed. By consideration of the possible transition states dur-

ing the substitution reaction, it is possible that the compound of the form [LTc(CO)₃] may be the kinetic product. Due to the higher stability of a coordinated phosphine subsequent substitution of a CO is possible and the yielded products **19 – 21** are finally the thermodynamic ones. Trans influence phenomena has also to be considered when discussing substitution mechanism.

Substitution of mer-TcCl(CO)₃[P(C₆H₅)₃]₂ by pseudo-allyl ligands such as triazenido or formamidinato derivatives led to the substitution of one chloride and one CO if starting with the loss of one phosphine and the chloride is observed if starting with mer-TcCl(CO)₂[P(CH₃)₂(C₆H₅)]₃ [32]. Trans influence is clearly responsible for this behaviour and these experiments are in good agreement with our own observations.

Crystal structures of compound **19** and **20** could be resolved. In both compounds the Tc—N bond length trans to the Tc—P bond is significantly shorter than the two others. This data again indicates the strong trans influence of CO ligands and has been observed
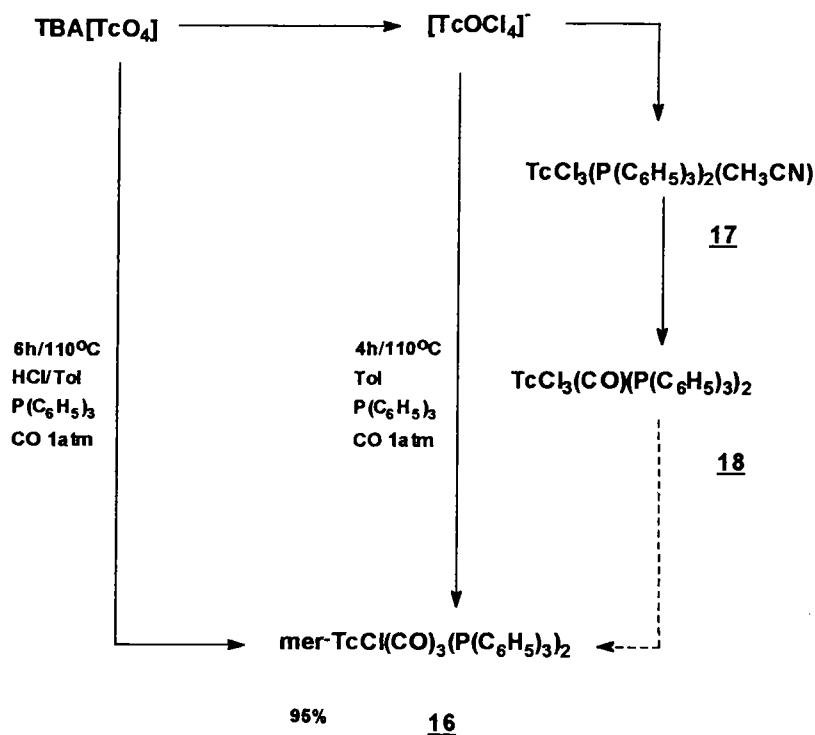
Fig. 10. Synthesis conditions for mer-TcCl(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$ using TBA[TcO$_4$] or TBA[TcOCl$_4$] as an educt.

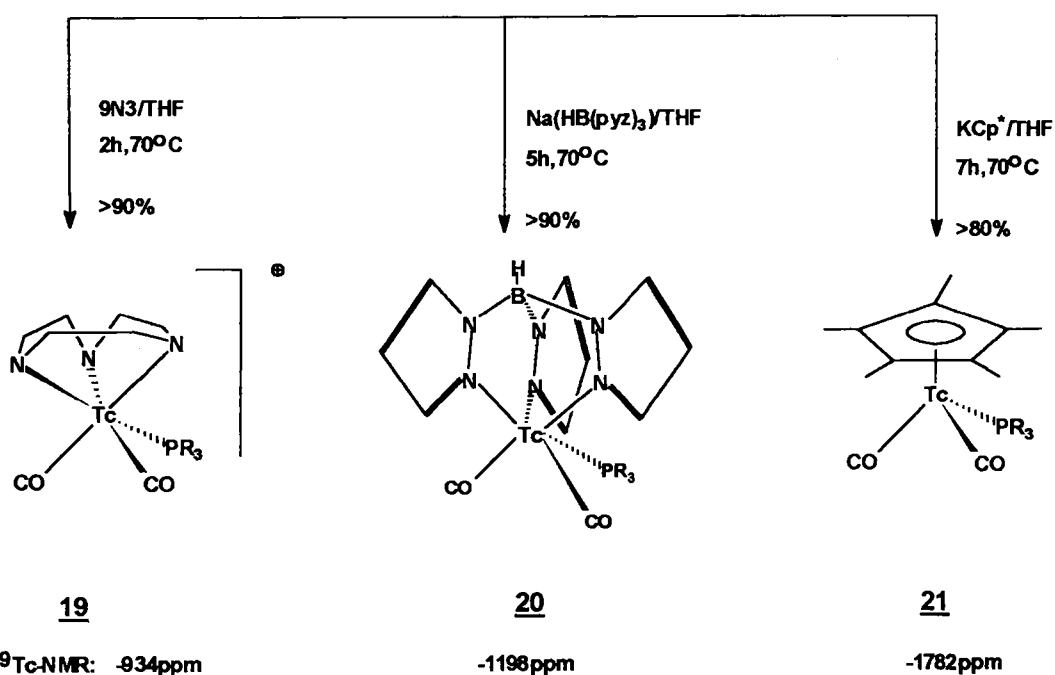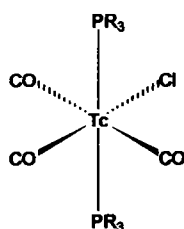**Fig. 11.** Substitution reactions on mer-TcCl(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$ using tridentate facial coordinating ligands.

in other systems as well. The Tc—P bond length in compound **20** is therefore significantly longer than in **19**. Trans influence of coordinated pyrazolyl is consequently stronger than for secondary amines.

Conclusion

Organometallic chemistry of technetium in high as well as in low oxidation states offers a lot of aspects not known from other elements. The synthesis of CH_3TcO_3 as well as substitution reactions are different from its rhenium analog owing to the significantly higher oxidation power of this complex. Its characterization and subsequent appliance to catalytic processes reveals new processes which do not take place for any of the other elements of the seventh triad. CH_3TcO_3 oxidizes alkene derivatives stereospecifically to cis 1,2 diols and thus is comparable to osmium but not to rhenium or manganese.

A new carbonylation of $NaTcO_4$ at moderate pressure yields selectively the Tc(I)-cluster **9** which proved to be a useful educt for substitution with facial coordinating tridentate ligands such as C_6H_6, HC_5Me_5 and ane-9N3. The cluster itself contains an isocarbonyl bonding to the sodium included in the cuban like structure. Similar synthesis with perrhenate yielded the same class of products but, as far as investigated, two and four nuclear species also. Reaction with technetium again takes place very much faster and under more moderate reaction conditions, again a sign that the higher oxidation potential offers a different behaviour also for low oxidation state. We emphasize that the synthesis of the technetium compound induced investigations with rhenium even though usually it is the other way round.

Carbonylation of $TBA[TcO_4]$ at one atmosphere CO pressure finally allowed access to mer-$TcCl(CO)_3[P(C_6H_5)_3]_2$ in quantitative yields. This important starting material can be used for many substitution reactions with tridentate facial coordinating ligands.

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