

MS43-P11 **Synthesis and Characterization of Novel Tantalum(V) and Niobium(V) Complexes containing N,O- and O,O'-Bidentate Ligands**, Renier Koen^a, Hendrik G. Visser^a & Andreas Roodt^a ^aDepartment of Chemistry, University of the Free State, South Africa.
Email: koen.renier87@gmail.com

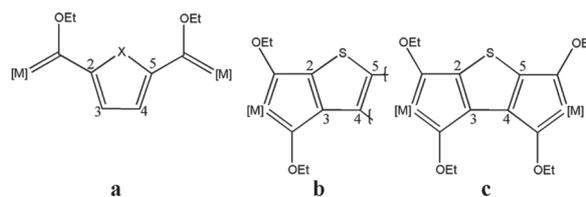
The separation of niobium and tantalum has always been a complicated process, particularly due to their near identical chemical properties. Niobium(V) and tantalum(V) are both hard metal centres and the halido species are known to readily hydrolyse [1]. In this present investigation of tantalum(V) and niobium(V) complexes, different bidentate ligands (*L,L'*-*Bid'*) have been used in synthesis, in an attempt to study the variation in activity and selectivity of coordination of *L,L'*-*Bid'* to tantalum -halides, -methoxides. (*L,L'*-*BidH* = acacH, tfaaH, hfaaH and tropH). Different synthetic procedures and characterization methods of these complexes will be discussed. Tantalum(V) and niobium(V) complexes of the type [Ta(X)₄(*L,L'*-*Bid*)] (X = halides, OMe and OEt; examples of *L,L'* = acetylacetonato (acac), dibenzoylmethanato (dbm) and tetramethylheptanedionato (thmd)), were synthesized and characterized by nuclear magnetic resonance spectroscopy (NMR) and infrared (IR) [2]. Moreover, single crystal X-ray diffraction was used to evaluate the characteristics of a range of complexes, and the results of the obtained structures containing mono- (halido and pseudo halido) and bidentate hard ligands *O,O'*- and *N,O'*- donor atoms will be presented and discussed [3]. A kinetic investigation of acacH coordination to solvated TaCl₅ is also presented. The reaction is defined by limiting kinetic behavior and is indicative of a two-step process. This involves the rapid formation of a proposed *trans*-[TaCl₂(OMe)₃(η¹-acacH)-intermediate]. Comparison of the forward rate constants for the two steps, *k*₁ and *k*₂ indicates that the first reaction is approximately six orders of magnitude (10⁶) faster than the second slower, rate determining step.

- [1] J. B. Lambert (2011). *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc., 1-23.
[2] Greenwood N. N., Earnshaw A., *Chemistry of the Elements*, 1997, 976.
[3] Basson, S. *Transition Met. Chem.*, 1982, 7, 207-209.
[4] Wendrup, P. *J. Mater. Chem.*, 2004, 14, 344-350.

Keywords: tantalum, separation, kinetics

MS43-P12 **Structures of Fischer multi-carbene complexes of furan and thiophene**. David C. Liles, Nina A. van Jaarsveld, Simon Lotz, Dept. of Chemistry, University of Pretoria, South Africa
E-mail: dave.liles@up.ac.za

Fischer type carbene complexes bound to five-membered heteroaromatic rings may be prepared by lithiating the ring followed by reaction with a metal carbonyl [M(CO)₆] and subsequent alkylation. The α-position protons on the rings are considerably more acidic than the β-position protons. Thus lithiation at the 2, or 2 and 5 positions is favoured leading to 2-monocarbene complexes or 2,5-biscarbene rod complexes (Fig. 1a). However, by blocking selected positions with substituents and / or by enhancing reactivity using thiophene (or its derivatives) brominated at selected sites, which allows for lithium-halogen exchange, the lithiation sites can be manipulated leading to chelated biscarbene complexes (Fig. 1b) [1] or a double chelated biscarbene complex (Fig. 1c) [2]. The structures of a number of chromium and tungsten biscarbene rod and chelate complexes have been studied and compared together with a few previously reported structures. The metal-carbene bond lengths in the chelated biscarbene complexes are slightly shorter than in the non-chelated complexes (average 2.032(9)Å v 2.082(3)Å for Cr, 2.162(7)Å v 2.201(9)Å for W) indicating a greater localization of the metal-carbene double bonds in the metallacycles. In the chelated biscarbene complexes (b), the metallacycles are approximately planar and coplanar with the thiophene rings. However, in the double chelated biscarbene complex (c) [3] steric crowding, particularly between the O atoms of the OEt substituents on the carbene C atoms ([C]) bonded to sites 3 and 4 of the thiophene ring, results in distortions in the metallacycle rings and in the coplanarity of the three-ring system, for example, the [C]-C3-C4-[C] torsion angle is 15(2)°. The distortions in the metallacycles result in a discrimination of the W-[C] bond lengths in each ring: 2.134(10)Å and 2.134(12)Å for [C] bonded to C2 or C5; 2.189(11)Å and 2.186(11)Å for [C] bonded to C3 or C4.



X = O, S; [M] = Cr(CO)₅, W(CO)₅ [M] = Cr(CO)₄, W(CO)₄ [M] = W(CO)₄

Fig. 1 furan and thiophene multi-carbene complexes

- [1] Lotz, S., van Jaarsveld, N. A., Liles, D. C., Crause, C., Görls, H. & Terblans, Y. M. (2012). *Organometallics* submitted.
[2] van Jaarsveld, N. A., Liles, D. C. & Lotz, S. (2010). *Dalton Trans.* **39**, 5777–5779.

Keywords: carbene complexes; chelates; molecular structure