COMMUNICATION

ChemComm
www.rsc.org/chemcomm

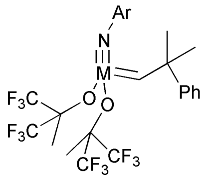
# Structure and reactivity studies of the first tungsten cyanoalkylidene complex†

**Thomas M. Cameron, A. Scott Gamble, Khalil A. Abboud and James M. Boncella***
*Department of Chemistry and Centre for Catalysis, University of Florida, Gainesville, FL, USA. E-mail: boncella@chem.ufl.edu*

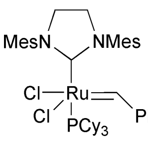
***Received (in Purdue, IN, USA) 28th February 2002, Accepted 4th April 2002***
***First published as an Advance Article on the web 25th April 2002***

**Alkylidene complex W(CHCMe$_2$Ph)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (Ar = 2, 6 diisopropylphenyl) (4) reacts with one equivalent of acrylonitrile in methylene chloride to afford the tetrameric, cyanoalkylidene complex [W(CHCN)(NAr)[OCMe(CF$_3$)$_2$]$_2$]$_4$ (5) which reacts with excess acetonitrile to give the tetrameric complex [W(N(H)C(CH$_3$)C(CN)C(CH$_3$)N)(NAr)[OCMe(CF$_3$)$_2$]$_2$]$_4$ (6).**

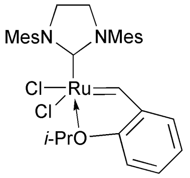
Metal catalyzed olefin metathesis has received considerable attention in recent years especially since the development of well-defined metal alkylidene catalysts.[1] One of the challenging tasks in this field involves efforts toward efficient cross-metathesis. The first reports to detail successful cross-metathesis were described by Crowe and co-workers and relied on judicious choice of terminal olefin substrates and Schrock's molybdenum alkylidene catalyst, Mo(CHCMe$_2$Ph)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**1**) (Ar = 2,6-diisopropylphenyl).[2] An important aspect of the work by Crowe's group was the observation that acrylonitrile participated in cross-metathesis reactions with terminal olefins when treated with catalytic amounts of **1**.[3] In a recent report, Blechert *et al.* detail the successful cross-metathesis of acrylonitrile and fluorinated terminal olefins using **2** and phosphine-free ruthenium alkylidene **3**.[4] Some reports have hinted at the lack of reactivity of acrylonitrile in cross-metathesis reactions using both molybdenum and ruthenium alkylidene catalysts.[5,6]



**1**, M = Mo
**4**, M = W



**2**



**3**

We have been interested in acrylonitrile cross-metathesis with α-olefins and were able to reproduce Crowe's initial results using **1** as the catalyst. We have also observed cross-metathesis between acrylonitrile and α-olefin 1-decene catalyzed by the ruthenium benzylidene **2**. We have determined that the purity of the acrylonitrile used in these reactions is of utmost importance in achieving high yields and reproducibility.[7] During our studies we also investigated the stoichiometric reactivity of W(CHCMe$_2$Ph)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**4**) with acrylonitrile. Although **4** is not an active catalyst for the cross-metathesis of acrylonitrile and α-olefins, it does react with acrylonitrile in a 1 : 1 ratio to afford the first tungsten cyanoalkylidene complex [W(CHCN)(NAr)[OCMe(CF$_3$)$_2$]$_2$]$_4$ (**5**).[8] Furthermore, complex **5** reacts with excess acetonitrile, giving tetrameric [W(N(H)C(CH$_3$)C(CN)C(CH$_3$)N)(NAr)[OCMe(CF$_3$)$_2$]$_2$]$_4$ (**6**), which is the first tetrameric diazatungstanacyclohexadiene. We herein report the solid-state structures of **5** and **6** and initial reactivity studies of **5**.

Complex **5** formed as X-ray quality crystals in 30% yield when **4** was treated with one eqivalent of acrylonitrile in methylene chloride solution without stirring.[7] A thermal ellipsoid plot of **5** is shown in Fig. 1.‡ Each tetramer has two unique tungsten atoms [W(1) and W(2)] that are symmetry related to the remaining two [W(1A) and W(2A)] through a $C_2$-axis. The geometry about W(1) is similar to W(2) and is best described as distorted trigonal bipyramidal. Each metal is linked to the other through a dative bond from the cyanoalkylidene nitrile nitrogen atom to an adjacent tungsten centre. The sum of the angles O(2)–W(1)–N(3), N(3)–W(1)–C(1) and C(1)–W(1)–O(2) is 357.9°, which defines the equatorial plane for this five coordinate W(1) centre and places the imido, alkylidene and alkoxide ligands in the equatorial plane. The axial ligands around W(1) consist of an alkoxide and the datively bound nitrogen [N(2)] from the nitrile functionality, with the N(2)–W(1)–O(1) angle being 161.3(2)°. The tungsten alkylidene bond lengths of 1.954(6) and 1.948(7) Å for W(1)–C(1) and W(2)–C(3), respectively, are similar and compare well with those reported for related trigonal bipyramidal monomeric alkylidene complexes. For example, the W=C length in the quinuclidine adduct *anti*-W(*trans*-CHCH=CHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quinuclidine) is 1.942(6) Å.[9] It can also be noted that the arrangement of ligands in *anti*-W(*trans*-CHCH=CHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quinuclidine) (equatorial imido, alkyli-

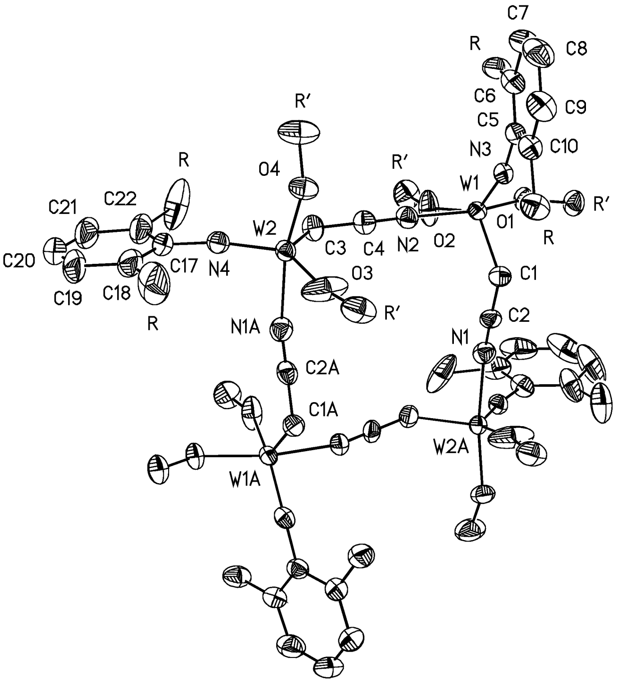


**Fig. 1** Thermal ellipsoid plot of **5** (50 % probability thermal ellipsoids). Selected bond lengths (Å) and angles (°) (R = *i*-Pr; R′ = OC(CH$_3$)(CF$_3$)$_2$; hydrogen atoms have been removed for clarity): W(1)–C(1) 1.954(6), W(1)–N(3) 1.735(5), W(1)–N(2) 2.148(5), W(2)–C(3) 1.948(7), W(2)–N(4) 1.734(5), W(2)–N(1A) 2.151(6), C(1)–C(2) 1.405(9), C(3)–C(4) 1.379(9), N(1)–C(2) 1.154(8), N(2)–C(4) 1.161(8); O(2)–W(1)–N(3) 140.3(3), N(3)–W(1)–C(1) 98.8(3), C(1)–W(1)–O(2) 118.8(3), N(2)–W(1)–O(1) 161.3(2), N(4)–W(2)–C(3) 98.9(3), C(3)–W(2)–O(3) 126.3(4), O(3)–W(2)–N(4) 132.9(3).

---

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b202110b/

DOI: 10.1039/b202110b

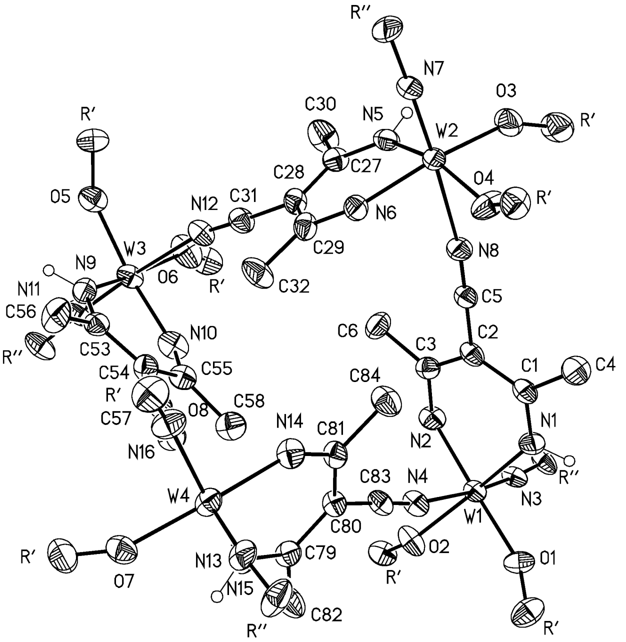
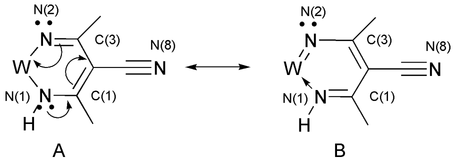


**Fig. 2** Thermal ellipsoid plot of **6** (50 % probability thermal ellipsoids). Selected bond lengths (Å) and angles (°) (R = *i*-Pr; R′ = OC(CH$_3$)(CF$_3$)$_2$; R″ = Ar; hydrogen atoms have been removed for clarity): W(1)–N(3) 1.748(6), W(1)–N(1) 2.092(6), W(1)–N(2) 1.904(7), W(1)–N(4) 2.304(6), N(2)–C(3) 1.303(9), N(1)–C(1) 1.319(9), C(2)–C(3) 1.422(11), C(1)–C(2) 1.425(11), C(2)–C(5) 1.417(10), C(5)–N(8) 1.169(9); W(1)–N(2)–C(3) 140.8(6), W(1)–N(1)–C(1) 131.3(6).

dene and axial quinuclidine) is similar to the arrangement at each metal centre in **5**.

Although complex **5** is insoluble in several conventional NMR solvents ($C_6D_6$, $CDCl_3$ and $CD_2Cl_2$) it dissolves when treated with $CD_3CN$. The $^1$H NMR of this solution is difficult to interpret due to extremely broadened resonances, and it is difficult to determine if **5** has been broken-up by coordination of acetonitrile to each tungsten centre. When the NMR tube containing **5** in $CD_3CN$ was allowed to sit in a glove box for several weeks, reaction with acetonitrile occurred and X-ray quality crystals‡ of **6** precipitated from solution.

Complex **6** crystallizes within a triclinic unit cell, and the tungsten atoms are arranged in a tetrahedral array. The molecule has a pseudo $C_2$-axis, and the thermal ellipsoid plot of **6**, shown in Fig. 2, views **6** along this axis. The alkylidene ligand in **5** has clearly reacted with acetonitrile to generate the tetrameric diazatungstanacyclohexadiene **6**. In complex **6** the geometry at each metal centre is best described as distorted octahedral. Bridging nitrile units link the metal centres and the bridging nitriles are always *trans* to an aryl imido group. These bridging nitrile functionalities are presumably those that linked the metal centres in **5**, and the alkylidene carbons from **5** now occupy part of the planar diazatungstanacyclohexadiene ring as carbons C(2), C(28), C(54) and C(80). The W(1)–N(1) bond length of 2.092(6) Å is significantly longer than the W(1)–N(2) distance of 1.904(7) Å. The corresponding W(1)–N(1)–C(1) and W(1)–N(2)–C(3) bond angles of 131.3(6) and 140.8(6)°, respectively, are also significantly different. We propose that this difference in bonding can be partially explained by invoking some contribution to bonding from bent imido B in Scheme 1. Placing imido character at N(2) in this fashion would shorten the W(1)–N(2) distance with respect to the W(1)–N(1) distance as well as make the W(1)–N(2)–C(3) angle more obtuse than the W(1)–N(1)–C(1) angle. The W(1)–N(4) bond length of 2.304(6) Å is typical for a dative bonding interaction, and the W(1)–N(3) distance of 1.748(6) Å is within the expected range for a metal–imido bond.[9] Although there is no rigorous symmetry in **6**, the coordination sphere about each metal centre is very similar to that discussed above for W(1).



**Scheme 1**

Similar reactivity has been observed for methylidenetitanocene and acetonitrile.[10] We propose that **6** forms *via* a mechanism similar to that in the literature in which acetonitrile reacts with the cyanoalkylidene giving an azametallacyclobutene. This intermediate inserts another acetonitrile into the W–C bond giving a diazametallacyclohexa-1,4-diene that tautomerizes to the observed structure. The reactivity of **5** with the nitrile functionality is in part responsible for the lack of cross-metathesis activity of **4** with acrylonitrile and appropriate olefins.

When a heterogeneous mixture of **5** in $CD_2Cl_2$ was treated with one equivalent of $PMe_3$ the crystals of **5** disappeared from the mixture and two alkylidene resonances appeared in the $^1$H NMR spectrum of the solution at room temperature [10.12 ppm (br), 9.96 ppm (d, $^3J_{H-P}$ = 6 Hz)]. A thorough analysis of this sample *via* variable temperature and 2D multinuclear NMR spectroscopy supports the formulation of these compounds as five coordinate alkylidene complexes of the type W(CHCN)(PMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**7**) for which there is precedence in the literature.[9] Unfortunately, we were unable to unambiguously assign an overall geometry to these alkylidene species. Treating this sample of **7** with one equivalent of benzaldehyde gave *trans*-cinnamonitrile as an organic product demonstrating that **7** behaves in a manner consistent with that of a Group 6 alkylidene.[7]

We acknowledge the National Science Foundation and the University of Florida for funding the purchase of X-ray equipment and B. P. Amoco for financial support of this work.

## Notes and references

‡ *Crystal data*: for **5**: $C_{88}H_{96}F_{48}N_8O_8W_4$, $M$ = 3041.13, monoclinic, space group $C2/c$, $a$ = 29.517(9), $b$ = 12.674(4), $c$ = 29.558(9) Å, $V$ = 11056(6) Å$^3$, $Z$ = 4, $\mu$(Mo-K$\alpha$) = 4.282 mm$^{-1}$, $T$ = 173(2) K, final $R1$ ($I > 2\sigma$) = 0.0418, $wR2$ ($I > 2\sigma$) = 0.1090, GOF (on $F^2$) = 1.075. For **6**: $C_{104}H_{116}F_{48}N_{16}O_8W_4$, $M$ = 3365.53, triclinic, space group $P\bar{1}$, $a$ = 19.308(2), $b$ = 20.222(2), $c$ = 21.243(2) Å, $V$ = 7637(2) Å$^3$, $Z$ = 2, $\mu$(Mo-K$\alpha$) = 3.109 mm$^{-1}$, $T$ = 193(2) K, final $R1$ ($I > 2\sigma$) = 0.0577, $wR2$ ($I > 2\sigma$) = 0.1559, GOF (on $F^2$) = 1.077.

CCDC reference numbers 180734 and 180735. See http://www.rsc.org/suppdata/cc/b2/b202110b/for crystallographic data in CIF or other electronic format.

1 For recent reviews see: R. R. Schrock, *Tetrahedron*, 1999, 8141; R. H. Grubbs and S. Chang, *Tetrahedron*, 1998, 4413.

2 W. E. Crowe and Z. J. Zhang, *J. Am. Chem. Soc.*, 1993, **115**, 10 998; W. E. Crowe, D. R. Goldberg and Z. J. Zhang, *Tetrahedron Lett.*, 1996, **37**, 2117.

3 W. E. Crowe and D. R. Goldberg, *J. Am. Chem. Soc.*, 1995, **117**, 5162.

4 S. Randl, S. Gessler, H. Wakamatsu and S. Blechert, *Synlett*, 2001, **3**, 430.

5 D. S. La, E. S. Sattely, J. G. Ford, R. R. Schrock and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2001, **123**, 7767.

6 A. K. Chatterjee, J. P. Morgan, M. Scholl and R. H. Grubbs, *J. Am. Chem. Soc.*, 2000, **122**, 3783.

7 See the ESI† for full experimental details.

8 Reactions of acrylonitrile with **1** gave intractable mixtures by $^1$H NMR spectroscopy.

9 R. R. Schrock, W. E. Crowe, G. C. Bazan, M. DiMare, M. B. O'Regan and M. H. Schofield, *Organometallics*, 1991, **10**, 1832.

10 K. M. Doxsee and J. B. Farahi, *J. Chem. Soc., Chem. Commun.*, 1990, 1452; K. M. Doxsee, J. B. Farahi and H. Hope, *J. Am. Chem. Soc.*, 1991, **113**, 8889; K. M. Doxsee, J. K. M. Mouser and J. B. Farahi, *Synlett.*, 1992, 13; J. Barluenga, C. del Pozo Losada and B. Olano, *Tetrahedron Lett.*, 1992, **33**, 7579; N. A. Petasis and D.-K. Fu, *Organometallics*, 1993, **12**, 3776.