

JOM 23595PC

## Preliminary Communication

### Synthesis and reaction of ( $\eta^5$ -pentamethylcyclopentadienyl)-bis(allyl)tantalum(III) complexes; crystal structure of Ta( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-( $\eta^3$ -1-phenylallyl)<sub>2</sub>

Kazushi Mashima, Yoshimichi Yamanaka, Yoshihiko Gohro and Akira Nakamura

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)

(Received February 5, 1993; in revised form February 12, 1993)

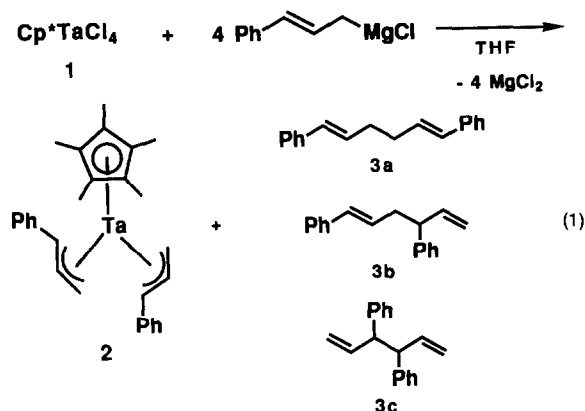
#### Abstract

We report here the synthesis and X-ray structure of a mononuclear 16-electron ( $\eta^5$ -pentamethylcyclopentadienyl)bis(allyl)-tantalum complex, Cp\*Ta( $\eta^3$ -PhC<sub>3</sub>H<sub>4</sub>)<sub>2</sub> (**2**). Carbonylation of **2** induced the coupling reaction with phenylallyl groups bound to tantalum to give 1,6-diphenyl-1,5-hexadiene and carbonyltantalum complexes. Oxidation of **2** with one-electron oxidants, DDQ and TCNQ, gave the tantalum(IV) complexes, [Cp\*Ta(PhC<sub>3</sub>H<sub>4</sub>)<sub>2</sub>]<sup>+</sup>[oxidant]<sup>-</sup>.

Although many kinds of transition metal-allyl complexes have been prepared, only a few allyl tantalum complexes have been reported [1–6]. Here we describe the synthesis of mononuclear 16-electron ( $\eta^5$ -pentamethylcyclopentadienyl)-bis(allyl)tantalum(III) complexes and elimination reactions of the two allyl groups from tantalum(III).

Treatment of Cp\*TaCl<sub>4</sub> (**1**) (Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) with 4 equiv. of allylMgCl gave a dark green compound of the empirical formula Cp\*Ta(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub> in 3% yield [7]. However, the reaction of **1** with 4 equiv. of 1-phenylallylMgBr in THF afforded complex Cp\*Ta( $\eta^3$ -PhC<sub>3</sub>H<sub>4</sub>)<sub>2</sub> (**2**) as red-brown crystals in 56% yield (eqn. (1)) [8], which is, to our knowledge, the first example of a mononuclear 16-electron ( $\eta^5$ -pentamethylcyclopentadienyl)-bis(allyl)tantalum complex.

The X-ray study [9] of a single crystal obtained from a saturated solution in a mixture of toluene and hexane revealed the structure shown in Fig. 1. The orientation of the two  $\eta^3$ -allyl moieties indicates that **2** is a



supine-supine isomer [10]. The analogous paramagnetic complexes CpM( $\eta^3$ -allyl)<sub>2</sub>, M = Cr and Mo, adopt a similar arrangement [11]. The coordination around tantalum of **2** approximated to two-legged piano-stool geometry. The hydrogen atoms attached to C3 and C13 are fairly close (2.50 Å) to the tantalum atom, which stabilizes the 16 electron species via agostic interaction [12,13]. The Ta–C(3 or 13)–H angles (91–96°) and the small coupling constant *J*(C–H) (145 Hz) also indicate the interaction [14]. The angle between the two planes

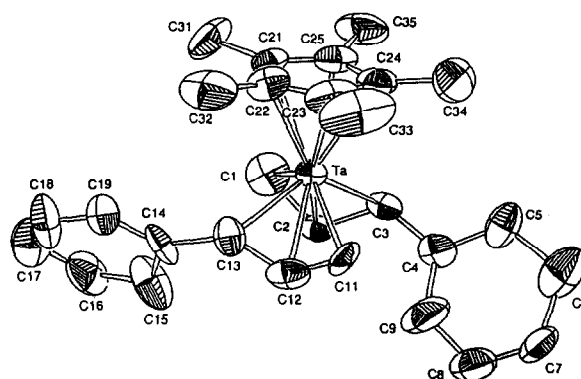
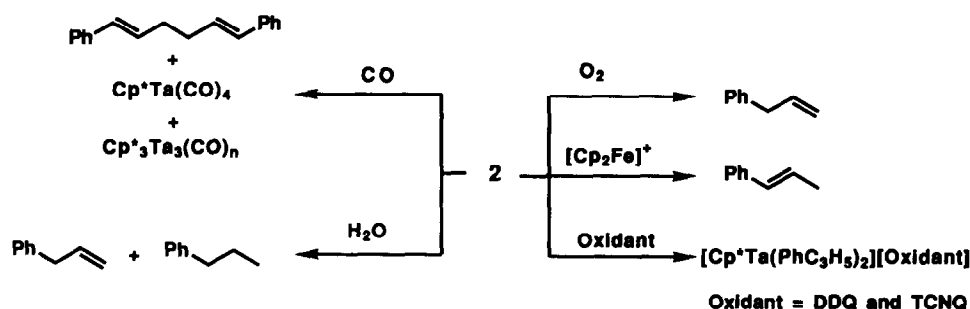


Fig. 1. ORTEP drawing of **2** with labelling scheme. Selected bond distances (Å) and angles (deg); Ta–C1 2.17(2), Ta–C2 2.25(3); Ta–C3 2.32(2); Ta–C11 2.29(2); Ta–C12 2.27(3), Ta–C13 2.27(2), C1–C2 1.49(3) C2–C3 1.46(3), C11–C12 1.28(4); C12–C13 1.41(4); C1–C2–C3 114(2), C11–C12–C13 123(2). The distances between the tantalum atom and the carbon atoms of the cyclopentadienyl moiety are in the range 2.37(3)–2.46(3) Å.

Correspondence to: Professor A. Nakamura.



Scheme 1.

of allyl groups is  $24.9^\circ$ , which is comparable to that ( $25.6^\circ$ ) of  $\text{CpMo(allyl)}_2$  [11b].

The reaction of  $\text{Cp}^*\text{TaCl}_4$  with 1-phenylallylMgBr, in addition to **2**, gives three isomers formed by coupling of the allyl groups, *i.e.* 1,6-diphenyl-1,5-hexadiene (**3a**), 1,4-diphenyl-1,5-hexadiene (**3b**), and 3,4-diphenyl-1,5-hexadiene (**3c**) (8 : 1 : 4 ratio), which were isolated in 42% yield. Such reductive coupling is rather rare for early transition metal organometallic compounds, though intramolecular coupling of two pentadienyl ligands bound to niobium has been reported [15].

Preliminary results on the reactivity of complex **2** are as follows. As a formally 16e complex, **2** might be expected to react with donor molecules, but the NMR spectra of **2** did not change in the presence of donor molecules such as trimethylphosphine or pyridine. However, reaction of **2** with smaller ligand carbon monoxide (50 kg/cm<sup>2</sup>) induced reductive coupling of the allyl groups [11b,11d] affording predominantly **3a** in 87% yield together with  $\text{Cp}^*\text{Ta(CO)}_4$  (13%) [16] and  $\text{Cp}_3^*\text{Ta}_3(\text{CO})_n$  ( $\nu(\text{CO})$  1943 and 1862 cm<sup>-1</sup>). Compound **3a** may be formed selectively via an intermediate,  $\text{Cp}^*\text{Ta(CO)}_n(\eta^1\text{-3-phenylallyl})_2$ , which undergoes reductive elimination to give **3a** and carbonyl tantalum complex.

Hydrolysis of complex **2** by the addition of degassed water (50 equiv) in benzene-*d*<sub>6</sub> resulted in the quantitative formation of a 1:1 mixture of 3-phenyl-1-propene and 1-phenylpropane. The strong oxophilic property of tantalum induces the cleavage of the H–O bond to form a hydrido-oxo-tantalum species [17], which is responsible for the reduction of the C=C double bond. When the reaction was carried out with D<sub>2</sub>O in the same conditions, the products were 3-deutero-3-phenyl-1-propene and 1,2,3-trideutero-1-phenylpropane [18].

A salient feature of the reactivity of **2** is the oxidatively induced release of an allyl moiety coordinated to tantalum. Treatment of **2** with an excess of dioxygen resulted in the formation of 3-phenyl-1-propene (48% yield), presumably formed by elimination of an allyl

group with a hydrogen atom derived from the  $\text{Cp}^*$  ligand [19].

We examined one- or two-electron oxidation of **2** [20]. When **2** in benzene-*d*<sub>6</sub> was mixed with two equiv. of ferrocenium cation, the starting complex disappeared completely within a few min to give 1-phenyl-1-propene in 46% yield based quantitatively on **2** and ferrocene. The corresponding 1:1 reaction also gave ferrocene and 1-phenyl-1-propene in 43% yield.

In contrast, treatment of **2** in THF with the weaker one-electron oxidants DDQ and TCNQ gave the tantalum(IV) complexes **4a** (dark red microcrystalline solid, 64% yield) and **4b** (deep red microcrystalline solid, 90% yield) [21].

These unusual redox reactions seem to be characteristic of the organometallic chemistry of tantalum(III) complexes.

#### Acknowledgements

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 04217102 from the Ministry of Education, Science and Culture, Japan.

#### References

- G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter and H. Zimmermann, *Angew. Chem.*, **78** (1966); *Angew. Chem., Int. Ed. Engl.*, **5** (1966) 151.
- T. Kruck and H.-U. Hempel, *Angew. Chem.*, **83** (1971) 437; *Angew. Chem., Int. Ed. Engl.*, **10** (1971) 408.
- A. van Baalen, C.J. Groenenboom and H.J. de Liefde Meijer, *J. Organomet. Chem.*, **74** (1974) 245.
- P.R. Brown, F.G.N. Cloke and M.L.H. Green, *J. Chem. Soc., Chem. Commun.*, (1980) 1126.
- H. Yasuda, T. Arai, T. Okamoto and A. Nakamura, *J. Organomet. Chem.*, **361** (1989) 161.
- V.C. Gibson, G. Parkin and J.E. Bercaw, *Organometallics*, **10** (1991) 220.
- Mp 104–107°C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 4.62 (m, H<sub>2</sub>), 1.86 (s, Cp\*), 0.93 (m, H<sub>1syn</sub>), –0.79 (m, H<sub>1anti</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 12.01 (C<sub>3</sub>Me<sub>5</sub>, J(C–H) = 127 Hz), 54.05 (C<sub>1</sub>, J(C–H) = 149 Hz), 73.56

- (C<sub>2</sub>,  $J(\text{C-H}) = 170$  Hz), 101.28 (C<sub>5</sub>Me<sub>5</sub>) ppm; UV (THF)  $\lambda_{\text{max}}$  580 nm. The mass spectrum ( $m/z = 1197$ ) suggested that this complex has the trimeric structure [Cp<sup>+</sup>Ta(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>, although the precise structure is still unclear.
- 8 **2**: mp 150–153°C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 6.87$ – $7.23$  (aromatic protons), 5.64 (ddd, H<sub>2</sub>,  $J(1,2) = 9.6$  Hz,  $J(2,3_{\text{syn}}) = 9.4$  Hz,  $J(2,3_{\text{anti}}) = 9.5$  Hz), 1.74 (s, Cp<sup>+</sup>), 0.72 (dd, H<sub>1</sub>,  $J(1,3_{\text{anti}}) = 1.9$  Hz), 0.07 (ddd, H<sub>3<sub>syn</sub></sub>,  $J(3_{\text{syn}},3_{\text{anti}}) = 6.4$  Hz),  $-0.27$  (ddd, H<sub>3<sub>anti</sub></sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 124.0$ , 127.8, 127.9, and 128.6 (aromatic carbons), 116.86 (C<sub>5</sub>Me<sub>5</sub>), 76.71 (C<sub>2</sub>,  $J(\text{C-H}) = 168$  Hz), 73.69 (C<sub>1</sub>, 145 Hz), 62.91 (C<sub>3</sub>, 151 Hz), 11.71 (C<sub>5</sub>Me<sub>5</sub>, 126 Hz); mass spectrum (<sup>181</sup>Ta)  $m/z$ : 550 (M<sup>+</sup>); UV (THF)  $\lambda_{\text{max}}$  757 nm. Anal. Calcd. for C<sub>28</sub>H<sub>33</sub>Ta: C, 61.09; H, 6.09. Found: C, 61.19; H, 6.16%.
- 9 Crystal data for **2**: monoclinic, space group Cc;  $a = 21.996(5)$  Å,  $b = 8.995(4)$  Å,  $c = 16.863(5)$  Å,  $\beta = 135.85(1)^\circ$ ,  $V = 2324(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd}} = 1.573$  gcm<sup>-3</sup>,  $R = 0.026$ ,  $R_w = 0.029$  for 2753 observed reflections (Mo K $\alpha$  radiation) with  $I > 3\sigma(I)$ .
- 10 We have used supine or prone to distinguish the direction of diene coordinated to Group 5 metals. (a) H. Yasuka, K. Tatsumi, T. Okamoto, K. Mashima, K. Lee, A. Nakamura, Y. Kai, N. Kanehisa and N. Kasai, *J. Am. Chem. Soc.*, **107** (1985) 2410; (b) T. Okamoto, H. Yasuda, A. Nakamura, Y. Kai, N. Kanehisa and N. Kasai, *J. Am. Chem. Soc.*, **110** (1988) 5008.
- 11 Similar complexes of Group 6 metals have been reported: (a) P.W. Jolly, C. Krüger, C.C. Romão and M.J. Romão, *Organometallics*, **3** (1984) 936; (b) K. Angermund, A. Döhring, P.W. Jolly, C. Krüger and C.C. Romão, *Organometallics*, **5** (1986) 1268; (c) O. Andell, R. Goddard, S. Holle, P.W. Jolly, C. Krüger and Y.H. Tsay, *Polyhedron*, **8** (1989) 203; (d) R.J. Blau and U. Siriwardane, *Organometallics*, **10** (1991) 1627; (e) M.C. Azevedo, T.H. Brock, P.W. Jolly, A. Rufinska and G. Schroth, *Polyhedron*, **10** (1991) 459.
- 12 M. Brookhart, M.L.H. Green and L.-L. Wong, *Prog. Inorg. Chem.*, **36** (1988) 1.
- 13 Alternatively, the 1,3- $\sigma^2$ -2- $\eta^1$ -allyl structure was considered to explain the NMR spectral data of **2**. However, the presence of agostic interaction based on crystallographic study is consistent with the observed NMR data of **2**.
- 14 Recently, the  $\sigma^3$ -allyl structure (tantabicyclobutane) for Cp<sub>2</sub><sup>+</sup>Ta(C<sub>3</sub>H<sub>5</sub>) has been reported based on the fact that the high field chemical shifts and the relatively low  $J(\text{C-H})$  coupling constants (147–149 Hz) for the terminal and central carbons of the allyl group [6].
- 15 E. Melendez, A.M. Arif, A.L. Rheingold and R.D. Ernst, *J. Am. Chem. Soc.*, **110** (1988) 8703.
- 16 W.A. Herrmann, W. Kalcher, H. Biersach, I. Bernal and M. Creswich, *Chem. Ber.*, **114** (1981) 3558.
- 17 A. van Asselt, B.J. Burger, V.C. Gibson and J.E. Bercaw, *J. Am. Chem. Soc.*, **108** (1986) 5347.
- 18 3-Deutero-3-phenyl-1-propene and 1,2,3-trideutero-1-phenylpropane were determined by mass and NMR spectra.
- 19 S.T. Carter, W. Clegg, V.C. Gibson, T.P. Kee and R.D. Sanner, *Organometallics*, **8** (1989) 253; M. Booji, A. Meetsma and J.H. Teuben, *Organometallics*, **10** (1991) 3246; A.D. Horton, *Organometallics*, **11** (1992) 3271 and references cited therein.
- 20 S.C.H. Ho, D.A. Straus and R.H. Grubbs, *J. Am. Chem. Soc.*, **106** (1984) 1533; W. Tumas, D.R. Wheeler and R.H. Grubbs, *J. Am. Chem. Soc.*, **109** (1987) 6182; R.H. Grubbs and W. Tumas, *Science*, (1989) 907; M.J. Burk, W. Tumas, M.D. Ward and D.R. Wheeler, *J. Am. Chem. Soc.*, **112** (1990) 6133; M.J. Burk, D.L. Staley and W. Tumas, *J. Chem. Soc., Chem. Commun.*, (1990) 809.
- 21 **5a**: mp > 280°C; ESR  $g = 2.0037$  (solid, 25°C); Anal. Calcd for C<sub>36</sub>H<sub>33</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Ta(H<sub>2</sub>O)<sub>2</sub>: C, 53.15; H, 4.58; N, 3.44. Found: C, 52.75; H, 4.65; N, 3.39%.  
**5b**: mp > 280°C; ESR  $g = 2.0030$  (solid, 25°C); Anal. Calcd for C<sub>40</sub>H<sub>37</sub>N<sub>4</sub>Ta(H<sub>2</sub>O)<sub>4</sub>: C, 58.11; H, 5.49; N, 6.78. Found: C, 58.12; H, 5.15; N, 6.96%.