

Short communication

A hydridotantalum(V)-carborane analogue of Schwartz's reagent: synthesis and reactivity^{1,2}

 Michael A. Curtis, M.G. Finn^{*}, Russell N. Grimes³

Department of Chemistry, University of Virginia, Charlottesville, VA 22901, USA

Received 9 April 1997

Abstract

The dichlorotantalum metallacarborane $\text{CpCl}_2\text{Ta}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ (**1**) on treatment with LiAlH_4 in THF gave a hydridotantalum dimer $[\text{CpTa}(\text{H})(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]_2(\mu\text{-Cl})_2$ (**2**), which was found to undergo alkyne insertion with *p*-tolyl acetylene to generate exclusively *trans*- $\text{CpCl}(\text{p-MeC}_6\text{H}_4\text{-CH=CH})\text{Ta}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ (**3**); the reaction of the latter complex with anhydrous HCl afforded *p*-tolylstyrene and **1**. In contrast, reaction of **2** with diphenyl acetylene or methyl phenyl acetylene gave hydridotantalum-alkyne complexes, which are apparently the first examples of alkyne π -coordination to a formal d^0 metal. Treatment of **2** with styrene produced the alkyl-tantalum species $\text{CpTaCl}(\text{CH}_2\text{CH}_2\text{Ph})(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ (**5**), but no reactivity was observed between **2** and the sterically hindered olefins *cis*-stilbene, *trans*-stilbene, and cyclohexene. Addition of anhydrous HCl to **5** generates **1** and styrene via an apparent β -elimination mechanism. © 1998 Elsevier Science S.A.

Keywords: Carboranes; Metallacarboranes; Tantalacarboranes; Tantalum; Hydridometallacarboranes

1. Introduction

The insertion of alkenes and alkynes into the Zr–H bond of $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (Schwartz's reagent) to form alkyl- or alkenylzirconium(IV) complexes (Cp_2ZrClR) is well documented [2–5].⁴ Treatment of these complexes with electrophiles such as HCl or *n*-bromosuccinimide (NBS) cleaves the Zr–C bonds and liberates the organic product in high yield [2,3]; in the alkenylzirconium species, retention of the C=C stereochemistry is observed [2]. Transmetalation reactions allow the generated alkyl or

alkenyl fragment to be used in a variety of ways for organic synthesis (⁴).

The Group 5 metallacarborane $\text{CpCl}_2\text{Ta}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ (**1**), was recently prepared in our laboratories [10,11], and we recognized that substitution of one of the Cl ligands with H in this complex would create a Ta(V) analogue of Schwartz's reagent in which one C_5H_5^- ligand is replaced by $\text{Et}_2\text{C}_2\text{B}_4\text{H}_4^{2-}$. Such a complex might well exhibit potentially useful differences in reactivity from Schwartz's reagent, and moreover could be readily tailored via regiospecific introduction of substituents at boron positions [12–14]. We present here the synthesis and initial reactivity studies of the first metallacarborane of this type.

2. Results and discussion

As shown in Scheme 1, reaction of **1** with LiAlH_4 in THF generated the dimer $[\text{CpTa}(\text{H})(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]_2(\mu\text{-}$

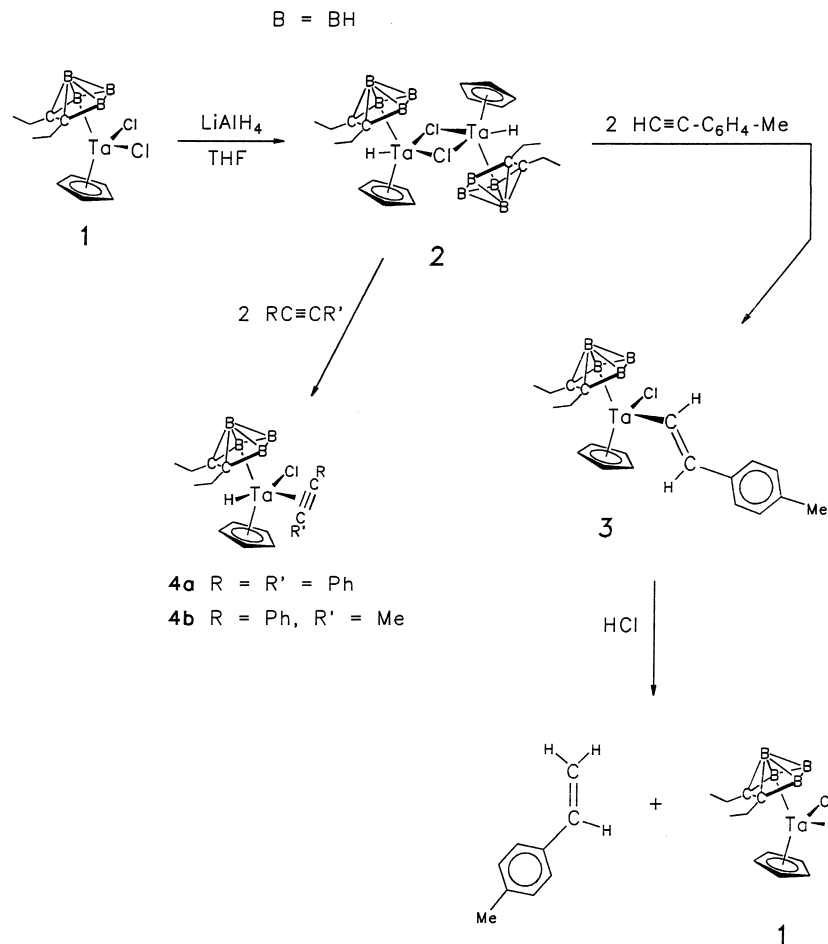
^{*} Corresponding author.

¹ Organotransition-Metal Metallacarboranes. 49. For part 48, see Ref. [1].

² Dedicated to Professor Kenneth Wade on the occasion of his 65th birthday.

³ Also corresponding author.

⁴ For synthetic applications of the Schwartz reagent, see Refs. [6–9].



Scheme 1.

$Cl)_2$ (2),⁵ which in contrast to Schwartz's reagent is soluble in THF and benzene at room temperature.

The product 2 is always accompanied by a smaller quantity of 1 in an approximate 7:3 ratio, and we have not yet found a satisfactory method for its removal. However, the presence of small amounts of 1 furnishes an internal standard for NMR observations, and control experiments on 1 have established that it is a nonparticipant in the reactions of 2 to be described. The hydride

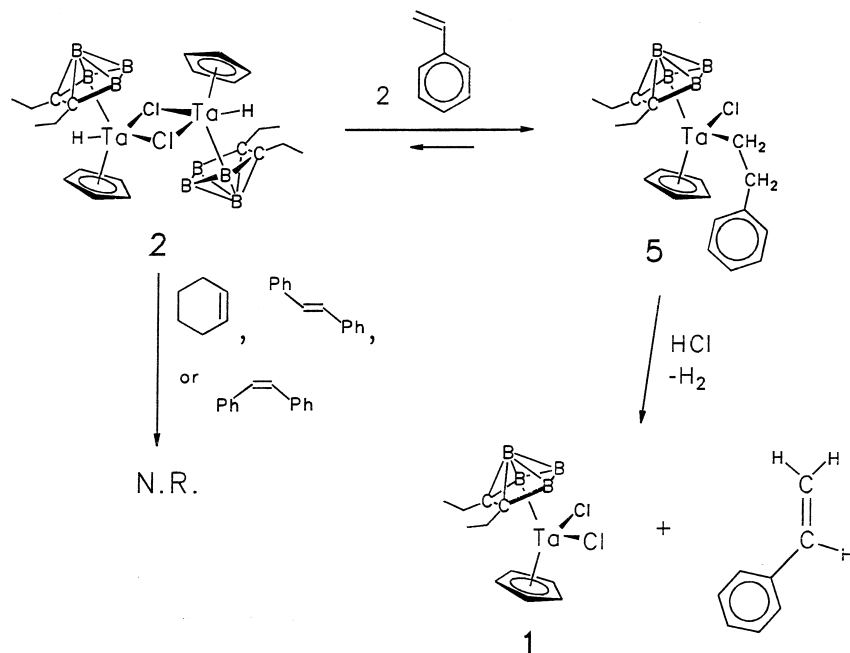
ligand on 2 is well defined by its IR band (ν_{Ta-H} 1839 cm^{-1}) and 1H NMR shift (δ_{Ta-H} 14.51 ppm).⁶

Treatment of 2 with 2.0 equivalent of 4-ethynyltoluene gave only the trans vinylic complex 3,⁷ indicating that Ta-H addition occurs in a cis fashion (Scheme 1); the vinyl proton shifts appear at doublets with $J_{H-H} = 18.6$ Hz at δ 7.39 and 6.68 ppm. In order to explore the steric effects of Ta-H addition to alkynes, 2 was reacted with 2.0 equivalent of diphenylacetylene. The expected vinylic species was not observed; instead,

⁵ Under a N_2 atmosphere the orange-air-stable complex 1 (500 mg, 1.12 mmol) was treated with 0.33 equivalent of $LiAlH_4$ (1 M in THF) in THF at $-78^\circ C$. The solution turned golden yellow as it warmed to room temp over 3 h. The solvent was removed in vacuo and the residue extracted with toluene. Removal of the toluene from the filtrate afforded 380 mg of a 30:70 mixture of 1 (72 mg) and 2 (308 mg). 1H NMR (300 MHz, C_6D_6 , δ): 14.51 (TaH, s, 2H), 5.36 (Cp, s, 10H), 2.92 (ethyl CH_2 , m, 4H), 2.62 (ethyl CH_2 , m, 2H), 2.44 (ethyl CH_2 , m, 2H), 1.44 (ethyl CH_3 , t, 6H, $J_{H-H} = 7.5$ Hz), 1.19 (ethyl CH_3 , t, 6H, $J_{H-H} = 7.5$ Hz). ^{13}C NMR (75.4 MHz, C_6D_6 , δ): 104.8 (Cp), 24.5 (ethyl CH_2), 23.7 (ethyl CH_2), 14.9 (ethyl CH_3), 14.3 (ethyl CH_3). IR (neat film, cm^{-1}): ν_{B-H} 2560, ν_{Ta-H} 1839. Mass spectrum: m/z 823 corresponding to the parent ion envelope.

⁶ In support of this assignment, the absorption at 1839 cm^{-1} is absent in the corresponding deuteride. The Ta-D band was not identified and is assumed to lie within the complex pattern of absorptions in the range 400 to 1500 cm^{-1} .

⁷ A 150 mg sample of a 30:70 mixture of 1 and 2 (122 mg, 0.148 mmol of 2) was dissolved in 1.5 ml of C_6D_6 , and 4-ethynyltoluene (34 mg, 0.296 mmol) was added at room temperature. 1H NMR (300 MHz, C_6D_6 , δ): 7.39 (vinyl H, d, 1H, $J_{H-H} = 18.6$ Hz), 7.11 (Ph, d, 2H, $J_{H-H} = 7.8$ Hz), 6.89 (Ph, d, 2H, $J_{H-H} = 8.8$ Hz), 6.68 (vinyl H, d, 1H, $J_{H-H} = 18.6$ Hz), 5.50 (Cp, s, 5H), 3.00 (ethyl CH_2 , m, 2H), 2.65 (ethyl CH_2 , m, 1H), 2.34 (ethyl CH_2 , m, 1H), 2.00 (tolyl CH_3 , s, 3H), 1.20 (ethyl CH_3 , t, 3H, $J_{H-H} = 7.8$ Hz), 1.06 (ethyl CH_3 , t, 3H, $J_{H-H} = 7.8$ Hz).



Scheme 2.

the hydridotantalum–alkyne product $\text{CpTaCl}(\text{H})(\text{PhC}\equiv\text{CPh})(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ (**4a**) was obtained.⁸ Coordination of alkynes to Group 5 metals has precedent in bis(cyclopentadienyl)tantalum(III) and –niobium(III) dialkylacetylene complexes [15,16], but is highly unusual for d^0 early transition metal species. Characterization of **4a** included a ^1H – ^{13}C connectivity (HETCOR) study, which revealed no carbon atom association with the ^1H NMR resonance at δ 9.23. The IR spectrum of **4a** exhibits bands at 1726 and 1807 cm^{-1} that are tentatively assigned to Ta–H and C=C stretches, respectively. The possibility of a Ta–H...B interaction cannot be discounted, since bridging between metal hydride ligands (e.g., Co–H, Fe–H, and Ru–H) and boron atoms in small metallocarboranes is well known [17]; this is conceivable in **2** but has not been demonstrated.

The stereochemistry of tantalacarborane–alkyne complexes was further explored via reaction of **2** with 3-phenylpropyne in benzene. As anticipated, two isomeric products were observed, in a ratio of 1:6 based on integration of Ta–H singlets in the ^1H NMR spectrum. If it is assumed that the favored configuration places the bulky phenyl group close to the Cl, while the smaller methyl substituent resides in the congested area near the Cp and carborane ligands, the predominant isomer can be tentatively assigned this geometry.

Addition of styrene to a benzene solution of **2** immediately generated the alkyltantalum complex $\text{CpTaCl}(\text{CH}_2\text{CH}_2\text{Ph})(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ (**5**),⁹ as shown in Scheme 2. However, no reactivity was observed with the sterically hindered olefins *cis*-stilbene, *trans*-stilbene, and cyclohexene. The sharp contrast with the facile formation of alkyne complexes **4a** and **4b** implies that complexation with tantalum is significantly depen-

⁸ A 150 mg sample of a 30:70 mixture of **1** and **2** (122 mg, 0.148 mmol of **2**) was dissolved in 1.5 ml of C_6D_6 , and diphenyl acetylene (52 mg, 0.296 mmol) was added at room temperature. The reaction was monitored by ^1H NMR and was complete in 13 h. ^1H NMR (300 MHz, C_6D_6 , δ): 9.35 (Ta–H, s, 1H), 7.67 (Ph, d, 2H, $J_{\text{H–H}} = 6.8$ Hz), 7.26 (Ph, d, 2H, $J_{\text{H–H}} = 7.8$ Hz), 7.06–6.91 (Ph, m, 6H), 5.29 (Cp, s, 5H), 2.77 (ethyl CH_2 , m, 1H), 2.57 (ethyl CH_2 , m, 1H), 2.30 (ethyl CH_2 , m, 1H), 2.15 (ethyl CH_2 , m, 1H), 1.16 (ethyl CH_3 , t, 3H, $J_{\text{H–H}} = 7.8$ Hz), 1.00 (ethyl CH_3 , t, 3H, $J_{\text{H–H}} = 7.8$ Hz). ^{13}C NMR (75.4 MHz, C_6D_6 , δ): 141.4 (Ph, quaternary), 140.2 (Ph, quaternary), 131.2 (Ph), 130.3 (Ph), 127.8 (Ph), 127.7 (Ph), 127.0 (Ph), 126.7 (Ph), 102.7 (Cp), 28.3 (ethyl CH_2), 24.9 (ethyl CH_2), 15.1 (ethyl CH_3), 14.3 (ethyl CH_3). IR (neat film, cm^{-1}): $\nu_{\text{B–H}}$ 2574, $\nu_{\text{C=C}}$ 1807, $\nu_{\text{Ta–H}}$ 1726. Mass spectrum: m/z 589 corresponding to the parent ion envelope.

⁹ A 150 mg sample of a 30:70 mixture of **1** and **2** (122 mg, 0.148 mmol of **2**) was dissolved in 1.5 ml of C_6D_6 , and styrene (30 mg, 0.296 mmol) was added at room temperature. The formation of **5** occurred rapidly. ^1H NMR (300 MHz, C_6D_6 , δ): 7.23–7.17 (Ph, m, 5H), 5.62 (Cp, s, 5H), 3.09 (CH_2Ph , m, 1H), 2.88 (ethyl CH_2 , m, 1H), 2.77 (ethyl CH_2 , m, 1H), 2.72 (ethyl CH_2 , m, 1H), 2.69 (Ta– CH_2 , m, 1H), 2.46 (CH_2Ph , m, 1H), 2.34 (ethyl CH_2 , m, 1H), 1.61 (Ta– CH_2 , m, 1H), 1.35 (ethyl CH_3 , t, 3H, $J_{\text{H–H}} = 7.8$ Hz), 1.13 (ethyl CH_3 , t, 3H, $J_{\text{H–H}} = 7.8$ Hz). ^{13}C NMR (75.4 MHz, C_6D_6 , δ): 148.4 (Ph, quaternary), 128.8 (Ph), 128.2 (Ph), 125.9 (Ph), 110.5 (Cp), 62.0 (Ta– CH_2), 41.1 (CH_2Ph , 23.3 (ethyl CH_2), 22.8 (ethyl CH_2), 14.8 (ethyl CH_3), 14.5 (ethyl CH_3).

dent on the greater electron density available in alkyne vs. alkene moieties.

Treatment of compounds **3** and **5** with 1 equivalent of anhydrous HCl quantitatively released *p*-methyl styrene and styrene, respectively, and regenerated **1** in both cases.¹⁰ The reaction of **5** was investigated further via addition of 0.5 equivalent of anhydrous HCl to a mixture of **2** and **5**, which rapidly generated H₂ and converted all of the **2** to the dichloride **1**. After 12 h, ¹H spectroscopy revealed the formation of styrene accompanied by a small amount of the hydridotantalum complex **2**. These observations suggest that **5** initially undergoes β -elimination, generating **2** which reacts with HCl to produce **1** and H₂. Addition of excess HCl was found to drive the reaction to completion, with quantitative formation of styrene and **1**.

The interaction of **4a** with either anhydrous or aqueous HCl initially afforded an as yet unidentified organometallic product (the same species forming in both cases). In the aqueous system the Ta center facilitated the generation of a Ph₂Et₂C₄B₄H₄carborane, the formation and structure of which are currently under investigation.

3. Conclusion

The reactivity of the hydridotantalacarborane complex **2** is thus shown to differ significantly from that of the Schwartz reagent. The latter species performs facile hydrometalation of a wide variety of alkynes and alkenes [2–5] (³), whereas **2** engages in the same reaction only with terminal substrates. Complex **2** is unreactive with several 1,2-disubstituted olefins and forms stable coordination complexes with internal alkynes, which are unknown for d⁰ metallocene complexes of group 4.¹¹ Furthermore, the alkyl complex **5**, derived from **2**, apparently undergoes β -hydride elimination, which is

not common for neutral zirconocene derivatives. All of these observations suggest that, despite its formal d⁰ electronic configuration, the tantalum center in **2** is significantly more electron-rich than is the zirconium center of [Cp₂ZrHCl]_n, which is expected given the differences in electronegativity and orbital interactions characteristic of carborane ligands as compared to cyclopentadienyl fragments [18].

Acknowledgements

This work was supported by the National Science Foundation, Grant No. CHE 9322490.

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¹⁰ Compounds **3** and **5** were treated with 1 equivalent of HCl (1 M in diethyl ether) at 0°C in C₆D₆. The identities of the cleaved products were confirmed by NMR spectroscopy following addition of authentic samples.

¹¹ Complexes of the type Cp₂M(η^2 -RCCR) (M=Ti, Zr, Hf) may be described in terms of alkyne coordination to an M(II) center, or as M(IV) metallacyclopentene systems. In either case, these are fundamentally different from the alkyne complexes reported here.