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# Di-($\eta^5$-cyclopentadienyl)tantalum chemistry: reactions of the trihydride with acetylenes

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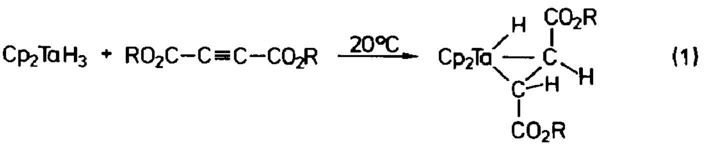
## Abstract

$Cp_2TaH_3$ reacts with the esters $RO_2C{\equiv}CCO_2R$ (R = Me, $SiMe_3$) at room temperature to give the fumaric ester complexes $Cp_2TaH$(*trans*-$RO_2CCH{=}CHCO_2R$). With simple acetylenes $RC{\equiv}CR$ (R = Me, $SiMe_3$, Ph), acetylene hydrides $Cp_2TaH$-($RC{\equiv}CR$) are formed. In the case of tolane (R = Ph), the presence of a *trans*-stilbene intermediate has been revealed by NMR spectroscopic monitoring of the reaction.

The reactions of the coordinatively saturated bent metallocene hydrides $Cp_2ReH$, $Cp_2MoH_2$, and $Cp_2WH_2$ with acetylenes have long been of interest [1,2]. In contrast, surprisingly little is known on the related reactions of the vanadium group trihydrides $Cp_2NbH_3$ and $Cp_2TaH_3$ [3]. We describe below some features of the $Cp_2TaH_3$ (I)/$RC{\equiv}CR'$ system. The starting material $Cp_2TaH_3$ can be readily made [4], and some C-alkyl derivatives of I have also been synthesized [5,6].

### Reactions with activated acetylenes

The trihydride I smoothly reacts with dimethyl acetylenedicarboxylate and bis(trimethylsilyl) acetylenedicarboxylate at room temperature to give the (olefin)hydride complexes II and III (eq. 1). Low temperature $^1H$ NMR monitoring of the reaction in toluene-$d_8$ over the temperature −80 to 30 °C did not reveal detectable intermediates. An excess of the acetylene reactant was used to complete the reaction, and no insertion of the acetylene into the Ta–H bond of II and III was observed. At 70 ° C paramagnetic species were formed, but were not investigated.



(II, R = Me;
III, R = $SiMe_3$)

(1)

Table 1

$^1$H NMR data [a]

| Compound | Cp rings | Ta–H | Other groups |
|---|---|---|---|
| II | 4.85s(5H), 4.69s(5H) | −0.07br(1H) | 3.59s($OCH_3$), 3.56s($OCH_3$), 2.63dd(1H) [b], 2.33d(1H), $^3J$ 12.3 Hz |
| III | 4.85s(5H), 4.69s(5H) | 0.12br(1H) | 0.37s(2 $SiMe_3$), 2.61dd(1H) [c], 2.33d(1H), $^3J$ 12.3 Hz |
| IV | 4.78d(10H), $^3J$ 0.4 Hz | −0.33br(1H) | 2.70q(Me), 2.53q(Me), $^5J$ 0.9 Hz [d] |
| V | 4.61s(10H), $^3J$ 0.3$_5$ Hz | −2.17br(1H) | 0.39s($SiMe_3$), 0.33s($SiMe_3$) |
| VI | 4.85d(10H), $^3J$ 0.5 Hz | 0.09br(1H) | 8.0–7.7m(4H), 7.5–7.0m(6H) |
| VII | 4.42s(5H), 4.31s(5H) | −1.53br(1H) | 8.0–7.7m(4H), 7.5–6.8m(6H) 3.29d(br)(1H), 2.74d(1H), $^3J$ 13.6 Hz |

[a] $\delta(^1H)$ (ppm), relative to internal TMS, 80 MHz, $C_6D_6$. [b] Additional coupling to Ta–H: $^3J$ 1.1 Hz. [c] Additional coupling to Ta–H: $^3J$ 1.0 Hz. [d] Coupling to Ta–H: $^4J$ < 0.2 Hz; decoupling of the Ta–H hydrogen slightly reduced the line width.

The new complexes have been characterized by elemental analyses (C, H), mass spectroscopy and NMR spectroscopy (Tables 1 and 2). The NMR spectra show the products II and III to possess $C_1$ symmetry, with two non-equivalent Cp rings, ester groups, and olefinic protons. Rotation of the olefinic ligand, which would result in interchange of the two ester groups and the two olefinic protons, is not observed. In the $^1$H NMR spectra one of the olefinic protons of II and III shows a small coupling with the hydridic proton of the Ta–H group; the hydridic proton showed only some broadening, but a double resonance experiment confirmed that it couples with the olefinic proton. The vicinal coupling constant $^3J(^1H-^1H)$ 12.3 Hz of the olefinic protons indicates that II and III are fumaric ester complexes, with the ester groups in *E* disposition. Earlier work gave a $^3J(^1H-^1H)$ value of 12.4 Hz for the (*E*)-cinnamic ester complex $Cp_2Mo(PhCH{=}CHCO_2CH_3)$ [7], while the acrylic ester

Table 2

$^{13}$ NMR data [a]

| Compound | Cp rings | Ta–C | | Other groups | |
|---|---|---|---|---|---|
| II | 96.0dquin, 95.5dquin<br>(179/6.$_7$) (179/6.$_7$) | 25.0dd,<br>(153/3.$_4$) | 23.9dm<br>(154) | 181.8m(CO), | 179.9q(CO)<br>(4) |
| | | | | 50.5q(MeO),<br>(145) | 50.3q(MeO)<br>(145) |
| III | 95.3dquin, 94.6dquin<br>(180/6.$_7$) (179/6.$_7$) | 26.6m,<br>(153) | 26.5$_5$m<br>(153) | 181.2m(CO), | 179.8dd(CO),<br>(5.$_6$/3.$_9$) |
| | | | | 0.2q($SiMe_3$),<br>(119) | 0.0q($SiMe_3$)<br>(119) |
| IV | 94.3dquin<br>(176/6.$_8$) | 143.6br, | 129.5br | 22.6qd(Me),<br>(125/5.$_8$) | 20.1q(Me)<br>(125) |
| V | 93.3dquin<br>(176/6.$_7$) | 167.9s, | 157.7br | 1.5qsept($SiMe_3$),<br>(119/2.$_0$) | 0.2qsept($SiMe_3$)<br>(119/2.$_0$) |
| VI | 95.6dquin<br>(177/6.$_6$) | 154.6br, | 145.9m | [b] | |

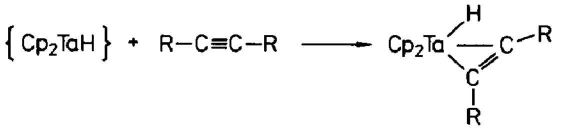
[a] $\delta(^{13}C)$ (ppm) relative to internal TMS, 67.88 MHz, $C_6D_6$; $J(^{13}C-^1H)$ (Hz) in parentheses. [b] See Experimental.

complex $Cp_2Mo(CH_2{=}CHCO_2CH_3)$ gave values of 12.0 and 9.3 Hz for the vicinal *trans* and *cis* coupling constants, respectively [7].

## Dihydrogen displacement reactions

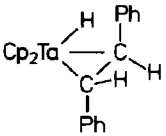
When heated [8,9] or irradiated [10,11] the trihydride I readily undergoes elimination of molecular dihydrogen to give a reactive 16e intermediate $Cp_2TaH$ (eq. 2). This intermediate reacts with various ligands, such as $PEt_3$ [8] or CO [11], to produce complexes of type $Cp_2TaH(L)$. In the case of alkynes this reaction (eq. 3) has been mentioned in two reports [6,12]. We have examined the reaction of I with 2-butyne, bis(trimethylsilyl)acetylene, and diphenylacetylene; on prolonged heating at 110–150 °C the (acetylene)hydride complexes IV–VI are formed, and can be isolated as air-sensitive solids.

$$\mathrm{Cp_2TaH_3} \xrightarrow{\Delta} \{\mathrm{Cp_2TaH}\} + \mathrm{H_2} \qquad (2)$$


(3)

(IV : R = Me ;
V : R = SiMe$_3$;
VI : R = Ph )

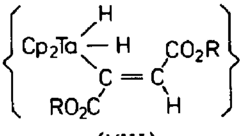
In the case of tolane, proton NMR experiments in toluene-$d_8$ revealed a second process. Whereas at 70 °C the tolane complex VI from the dihydrogen displacement reaction is the only complex formed, at 110 °C a mixture of VI and 30–65% of the *trans*-stilbene complex VII is formed within 24 h, and the trihydride I is almost completely consumed. On further heating for two weeks, VII reacts with the free tolane in the reaction mixture to give complex VI and free *trans*-stilbene.


(VII)

Irradiation of the bis(trimethylsilyl)acetylene complex V in benzene in the presence of diphenylacetylene slowly produces complex VI. This ligand substitution can be driven to completion by repeatedly removing the bis(trimethylsilyl)acetylene in a gentle vacuum.

## Discussion

The reactions of tantalocene trihydride with acetylenes fall into two classes. Activated acetylenes, containing electron-withdrawing substituents form (olefin)hydride complexes. This type of reaction has not previously been observed for I, but (olefin)hydride complexes of ethylene and other simple olefins are known [13–15]. The reaction is reminiscent of the reactions of $Cp_2MoH_2$ and $Cp_2WH_2$ with dimethyl acetylenedicarboxylate [1,2]; this suggests that the reaction involves a stereospecific *trans* insertion of the activated acetylene into the Ta–H bond to give an alkenyldihydride intermediate VIII and a subsequent rearrangement to the observed product. Unfortunately, the postulated intermediate VIII is still hypothetical.



(VIII)

In contrast, non-activated acetylenes form tantalocene (acetylene)hydride complexes. Although this reaction has been known for aliphatic acetylenes since 1974 [12], only solution data ($^1$H NMR and some IR data) have been published for these complexes [6,12]. Thus, compounds IV–VI seem to be the first fully described examples.

## Experimental

Experiments were carried out under nitrogen by Schlenk techniques. Toluene was distilled from sodium and hexane from K/Na alloy; oxygen was removed by repeated distillation under nitrogen.

*[$\eta^2$-(Dimethyl fumarate)]di-($\eta^5$-cyclopentadienyl)hydridotantalum (II)*

Dimethyl acetylenedicarboxylate (317 μl, 367 mg, 2.58 mmol) was added with stirring to a solution of I (390 mg, 1.24 mmol) in toluene (10 ml). The colour of the mixture quickly changed from pale yellow to red. After stirring at room temperature for 2 h, the volatiles were completely removed in vacuo. Addition of $Et_2O$ (40 ml) and stirring gave a light-brown solid which was filtered off, washed with $Et_2O$ (2 × 10 ml), and dried in vacuo (yield 0.22 g, 0.48 mmol, 39%); m.p. 149–150 °C, air-sensitive, slightly soluble in $Et_2O$, soluble in toluene and THF. Attempted chromatography on $Al_2O_3$ (7% $H_2O$) resulted in decomposition. Attempts to obtain crystalline samples were unsuccessful. Found: C, 41.96; H, 4.23. $C_{16}H_{19}TaO_4$ calc.: C, 42.12; H, 4.19%.

MS (70 eV): *m/e* ($I_{rel.}$) 456 (1; $M^+$), 342 (100; $Cp_2TaOCH_3{}^+$), 312 (85; $Cp_2TaH^+$), 311 (19; $TaCp_2{}^+$). IR (Nujol): $\nu$(Ta–H) 1734m, br (assignment verified by deuteration), $\nu$(CO) 1684vs, 1663vs $cm^{-1}$.

*[$\eta^2$-{Bis(trimethylsilyl) fumarate}]di-($\eta^5$-cyclopentadienyl)hydridotantalum (III)*

I (0.50 g, 1.59 mmol) in toluene (15 ml) was treated with $Me_3SiO_2CC{\equiv}CCO_2SiMe_3$ (0.91 ml, 0.90 g, 3.48 mmol) as described for II. Workup as above with hexane as solvent (30 ml) gave a light-orange solid which was removed by filtration, washed with hexane (2 × 5 ml), and dried in vacuo (yield 0.78 g, 1.36 mmol, 86%); m.p. 126–127 °C, > 135 °C dec. with evolution of gas, air-sensitive. Found: C, 41.72; H, 5.58. $C_{20}H_{31}TaO_4Si_2$ calc.: C, 41.95; H, 5.46%.

MS (70 eV, 125 °C): *m/e* ($I_{rel.}$) 572 (2; $M^+$), 402 (33; $Cp_2TaH_2OSi(CH_3)_3{}^+$), 401 (41; $Cp_2TaHOSi(CH_3)_3{}^+$), 400 (100; $Cp_2TaOSi(CH_3)_3{}^+$), 312 (41; $Cp_2TaH^+$), 311 (41; $TaCp_2{}^+$). IR (Nujol): $\nu$(Ta–H) 1768m (assignment verified by deuteration), $\nu$(CO) 1700s, 1685s $cm^{-1}$.

### *($\eta^2$-2-Butyne)di-($\eta^5$-cyclopentadienyl)hydridotantalum (IV)*

A yellow solution of trihydride I (0.98 g, 3.12 mmol) and 2-butyne (0.50 ml, 6.2 mmol) in toluene (20 ml) was heated under reflux for 6 d. Removal of all volatiles in vacuo, extraction of the residue with hexane (3 × 20 ml), and filtration of the extract gave a red solution, which was concentrated in vacuo at room temperature. Cooling to −70 °C gave a light-brown solid. The mother liquor was concentrated, and cooled again to give a second crop of IV (total yield 0.85 g, 2.32 mmol, 74%); m.p. 130–131 °C, dec. > 170 °C, can be sublimed with great losses (100 °C/$10^{-6}$ bar), very air-sensitive, soluble in toluene, $Et_2O$ and methanol. Found: C, 46.04; H, 4.70. $C_{14}H_{17}Ta$ calc.: C, 45.91; H, 4.68%.

MS (70 eV, 25 °C): $m/e$ ($I_{rel.}$) 366 (40; $M^+$), 312 (100; $Cp_2TaH^+$), 311 (36; $TaCp_2^+$). IR (Nujol): 1780s $cm^{-1}$.

### *[$\eta^2$-{Bis(trimethylsilyl)acetylene}]di-($\eta^5$-cyclopentadienyl)hydridotantalum (V)*

A solution of I (0.86 g, 2.74 mmol) and bis(trimethylsilyl)acetylene (0.67 ml, 0.51 g, 3.00 mmol) in toluene (25 ml) was kept at 110 °C for 15 d. Removal of the volatiles in vacuo and sublimation of the residue (100 °C/$10^{-6}$ bar) gave V (1.05 g, 2.18 mmol, 80%) as a lemon-yellow solid; m.p. 107–108 °C, air-sensitive. Found: C, 44.52; H, 5.98. $C_{18}H_{29}TaSi_2$ calc.: C, 44.80; H, 6.06%.

MS (70 eV): $m/e$ ($I_{rel.}$) 483 (2.5; $M^+$), 482 (10; $M-$H), 312 (100; $Cp_2TaH^+$), 311 (31; $TaCp_2^+$). IR (Nujol): 1757m, 1700m br, 1680m, 1657w $cm^{-1}$.

### *Di-($\eta^5$-cyclopentadienyl)($\eta^2$-diphenylacetylene)hydridotantalum (VI)*

A mixture of I (0.90 g, 2.86 mmol) and diphenylacetylene (1.52 g, 8.53 mmol) was kept at 150 °C for 3 h. The violet melt was triturated with hexane (25 ml) three times to give VI as a brownish gray solid. This was collected on a G3-frit, washed with hexane (3 × 10 ml), and dried in vacuo (yield 0.78 g, 1.59 mmol, 56%); m.p. 137–138 °C, air-sensitive, slightly soluble in hexane, soluble in toluene. Attempted chromatography on $Al_2O_3$ (7% $H_2O$) resulted in decomposition. Found: C, 58.54; H, 4.44. $C_{24}H_{21}Ta$ calc.: C, 58.78; H, 4.32%.

MS (70 eV): $m/e$ ($I_{rel}$) 490 (30; $M^+$), 346 (35; $CpTaC_2H_6H_3{}^+$), 312 (100; $Cp_2TaH^+$); 311 (15; $TaCp_2{}^+$). IR (Nujol): 1790w, 1774m, 1738s, 1590s $cm^{-1}$. $^{13}C$ NMR data for phenyl groups: 143.9m("quin") ($C_i$), 141.9t(7.$_6$) ($C_i$), 130.4dt (160/6.$_8$) ($C_o$), 129.4dt(161/6.$_8$) ($C_o$), 129.1dd(161/7.$_6$) ($C_m$), 128.5dd(160/7.$_7$) ($C_m$), 127.1dt(161/7.$_2$) ($C_p$), 125.9dt(160/7.$_8$) ($C_p$).

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