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Protonation of the d^2 tantalum complexes $Cp_2Ta(L)H$. Synthesis and structural studies of cationic dihydride complexes

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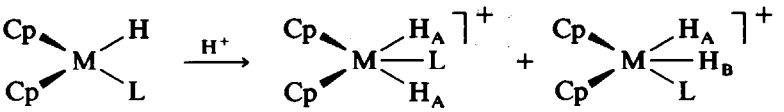
Abstract

Protonation of various d^2 tantalum complexes $Cp_2Ta(L)H$ ($L = PMe_2Ph$, $P(OMe)_3$) gives cationic species whose structures are dependent on L. A dihydrogen–dihydride equilibrium is assumed for $Cp_2Ta[P(OMe)_3)H_2]^+$.

Introduction

The basic properties of the d^2 monohydride complexes $Cp_2M(L)H$ (M = Nb, Ta; L = bielectronic ligand) towards Lewis acid organometallic fragment [1] or Brönsted acids [1a,2] are now well established. Spectroscopic data suggest the symmetrical structure α for two cationic protonated complexes $[Cp_2M(L)H_2]^+$, with the β toplogical isomer undetected.



(1) (α) (β)

Several examples of η^2-H_2 complexes prepared by protonation of hydridometal complexes have been reported [3], and formation of the dissymmetric structure β could obviously be of great interest in connection with the existence of non-classical hydrides. We therefore decided to investigate the behaviour of several tantalum derivatives $Cp_2Ta(L)H$ ($L = PMe_2Ph$ or $P(OMe)_3$) in an acidic medium, and present our results below.

Results and discussion

Protonation of the phosphine complex $Cp_2Ta(PMe_2Ph)H$ (2) gave a mixture of the two structural isomers α and β. The ^1H NMR spectrum reveals the presence of

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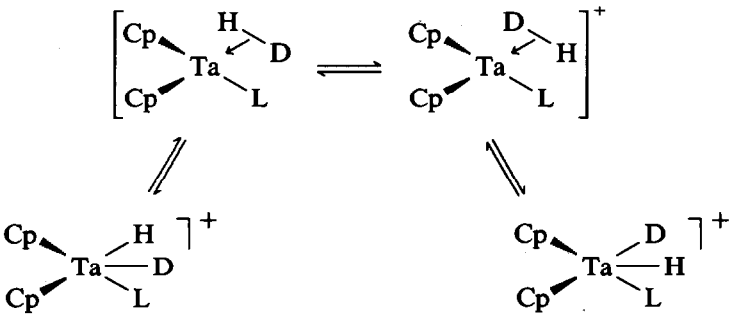
a slight excess of the dissymmetric structure β (60:40) that might be due to a H^+ preferential attack from the less hindered side of the $2a_1$ lateral orbital [4]. Besides the appropriate cyclopentadienyl and ligand resonances (see Experimental section) two distinct patterns appear in the resonance range of the metallic hydrogen belonging to the symmetrical **2**α (A_2X spin system, X = ^{31}P) and dissymmetrical **2**β (ABX spin system) isomers respectively. The data are listed in Table 1.

A more significant stereochemical induction occurred when the complex $Cp_2Ta[P(OMe)_3]H$ (**3**) was treated with HCl (**3**α/**3**β: 30/70). The high field ^{1}H NMR spectrum showed resonance patterns similar to those of **2**α + **2**β, but analysis of the ABX spin (Fig. 1) system revealed a value for $J(H_A-H_B)$ of 81.6 Hz. This coupling constant is quite surprisingly large compared with that of the related complex **2**β ($J(H_A-H_B) = 13.5$ Hz). In order to determine whether such a value could be assigned to an η^2-H_2 ligand in a pure from or in a dihydrogen–dihydride equilibrium, we measured a T_1 by the inversion recovery method; a T_1 value of 900 ms was obtained, consistent with a classical dihydride structure [5]. Another spectroscopic criterion for the presence of a dihydrogen ligand is the value of the H–D coupling [6] and so we tried to convert 3β into its isotopomer. Treatment of complex **3** with aqueous DCl afforded exclusively the structurally dissymmetric cation as a mixture (50:50) of centrally- and laterally-deuteriated compounds. Analysis of the NMR spectrum revealed a value for J(HD) of about 1 Hz.



The J(HD) and T_1 values indicate mainly a dihydrido structure. However, formation of the centrally deuteriated complex by a direct inside approach of D^+ seems unlikely, and the presence of an η^2-HD form, even to a minor extent, cannot be completely ruled out.

Experimental

Infrared spectra were recorded on Perkin–Elmer 580B spectrometer; ^{1}H and ^{31}P NMR spectra were recorded on a Jeol FX100 and a Bruker WM400 instruments, respectively.

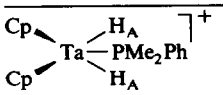
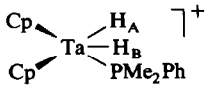
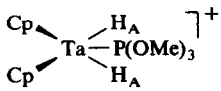
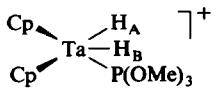
All reactions were carried out under dry argon, and the solvents were dried by standard methods and distilled before use.

Preparation of $Cp_2Ta(PMe_2Ph)H$ (2)

A slight excess (10%) of dimethylphenylphosphine was added to a suspension of 2.4 g (7.6 mmol) of Cp_2TaH_3 in decane (50 ml) and the mixture was kept at 140 °C for 3 h. The dark-colored mixture was evaporated, and the crude solid residue was

Table 1

^{1}H NMR data of complexes **2α**, **2β**, **3α** and **3β**

		^{1}H NMR (δ ppm/TMS; J Hz; CD_3COCD_3)	
		Ta–H_A	Ta–H_B
	**2α**	−0.44 (d, 2, J(P–H) = 71)	
	**2β**	−0.39 (m, 1, $J(H_A–P)$ = 11.5)	−0.89 (m, 1, $J(H_B–P)$ = 75.5)
		$J(H_A–H_B)$ = 13.5	
	**3α**	−1.51 (d, 2, J(P–H) = 86.2)	
	**3β**	−0.81 (m, 1, $J(H_A–P)$ = 10.4)	−1.93 (m, 1, $J(H_B–P)$ = 89.8)
		$J(H_A–H_B)$ = 81.6	

washed with pentane (2 × 20 ml). Yield 65%. An analytical pure sample was obtained by recrystallization (diethyl ether/pentane) as brown crystals.

^{1}H NMR (C_6D_6): δ 7.61–7.07 (10H, m, Ph); 4.33 (10H, dd, J(P–Cp) = 2.1, J(H–Cp) = 0.6 Hz, Cp); 1.37 (6H, d, J(P–Me) = 7 Hz, Me); −9.20 (1H, dm, J(H–P) = 20.4 Hz, TaH). ^{31}P{^{1}H} NMR (C_6D_6): δ +6.0 (s).

Preparation of $Cp_2Ta[P(OMe_3)_3]H$ (3)

According to the above procedure, complex **3** was obtained (55% yield) as orange crystals.

^{1}H NMR (C_6D_6): δ 4.51 (10H, d, J(Cp–P) = 2 Hz, Cp); 3.34 (9H, d, J(Me–P) = 11 Hz, Me); −8.95 (1H, d, J(H–P) = 22.7 Hz, TaH). ^{31}P{^{1}H} NMR (C_6D_6): δ +196 (s).

Preparation of $[Cp_2Ta(PMe_2Ph)H_2]^+PF_6^-$ (2α and 2β)

A 1 *M* solution of aqueous hydrochloric acid (3 ml) was added at room temperature to a brown suspension of $Cp_2Ta(PMe_2Ph)H$ (1.18 mmol) in THF (5 ml) and water (15 ml); the solid disappeared immediately after addition, and the THF-water solution became colourless. The solution was filtered and a solution of NH_4PF_6 (1.23 mmol) in water (5 ml) was added slowly at 0 °C. The THF was removed by evaporation under vacuum to leave the mixture of the two diastereoisomers **2α** and **2β** as a white solid. The precipitate was filtered off, washed with cold water, and dried under vacuum (overall yield about 85%).

The ^{1}H NMR spectrum of the mixture indicates a 60/40 ratio for the isomers **2α**/**2β**. Isomer **2α**: ^{1}H NMR (CD_3COCD_3): δ 8.00–7.60 (5H, m, Ph); 5.75 (10H, dt, J(P–H) = 1.2, J(H–H) = 0.35 Hz, Cp); 2.17 (6H, d, J(P–H) = 9.1 Hz, P*Me*$_2$Ph); −0.44 (2H, d, J(P–H) = 71 Hz, Ta*H*$_2$). ^{31}P{^{1}H} NMR (CD_3COCD_3) δ −5.6 (s). Isomer **2β**: ^{1}H NMR (CD_3COCD_3): δ 8.00–7.60 (5H, m, Ph); 5.72 (10H, d,

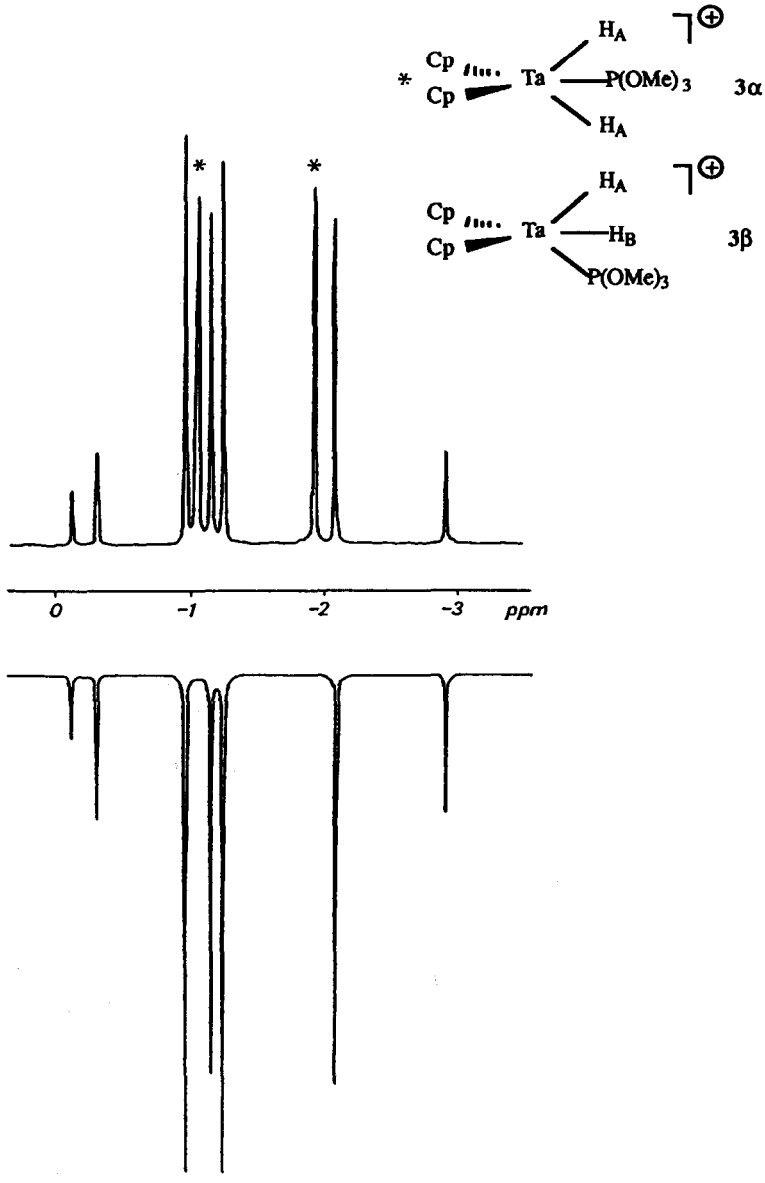


Fig. 1. ^{1}H NMR spectra of a mixture of 3α+3β in the hydride region (CD_3COCD_3; 100 MHz; TMS reference) on the top and computed spectrum of 3β on the bottom.

J(P–H) = 2.05 Hz, Cp); 2.14 (6H, d, J(P–H) = 9.5 Hz, PMe_2Ph); −0.39 (1H, m, J(P–H_A) = 11.5, J(H_A–H_B) = 13.5 Hz, Ta-H_A); −0.89 (1H, m, J(P–H_B) = 75.5, J(H_A–H_B) = 13.5 Hz, Ta–H_B). ^{31}P{^{1}H} NMR (CD_3COCD_3): δ 12.0 (s). IR (isomers 2α + 2β): ν(Ta–H) = 1795 cm^{-1} (Nujol).

Preparation of {$Cp_2Ta[P(OMe)_3]H_2$} + PF_6^- *(3α and 3β)*

Similarly isomers 3α and 3β were obtained in a 30/70 diastereoisomeric ratio. Isomer 3α: ^{1}H NMR (CD_3COCD_3): δ 5.92 (10H, m, Cp); 3.86 (9H, d, J(P–H) = 11

Hz, $P(OMe)_3$); −1.51 (2H, d, $J(P-H) = 86.2$ Hz, TaH_2). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 155.15 (s). Isomer 3β: ^1H NMR (CD_3COCD_3): δ 5.81 (10H, d, $J(P-H) = 1.95$ Hz, Cp); 3.99 (9H, d, $J(P-H) = 11$ Hz, $P(OMe)_3$); −0.81 (1H, m, $J(P-H_A) = 10.4$, $J(H_A-H_B) = 81.6$ Hz); −1.93 (1H, m, $J(P-H_B) = 89.8$, $J(H_A-H_B) = 81.6$ Hz).

$^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 160.6 (s). IR (isomers 3α + 3β): ν(Ta–H) = 1770 cm^{-1} (Nujol).

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