Surface Organometallic Chemistry of Inorganic Oxides: The Synthesis and Characterization of $(\equiv SiO)Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_2$ and $(\equiv SiO)_2Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)$

Véronique Dufaud, Gerald P. Niccolai, Jean Thivolle-Cazat, and Jean-Marie Basset*

Contribution from the Laboratoire de Chimie Organométallique de Surface, UMR 9986 CNRS-CPE, 2, avenue Albert Einstein, 69626 Villeurbanne cedex, France

Received April 15, 1994. Revised Manuscript Received November 21, 1994[®]

Abstract: The synthesis of two silica-supported tantalum(V) carbene complexes is reported. The reaction of $Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_3$ (**1**) with a silica dehydroxylated at 500 °C produces a mixture of $(\equiv SiO)Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_2$ (**2a**) and $(\equiv SiO)_2Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)$ (**2b**) and neopentane gas (on average 1.3 equiv/equiv of tantalum). The reaction of **2a/2b** with water produces 2.6 mol of neopentane. The reaction of **2a/2b** with acetone produces 1 equiv of 2,4,4-trimethyl-2-pentene per grafted tantalum, indicating that **2a,b** each bear one carbene ligand. When **1** is reacted with fully (>90%) deuterated silica, the product neopentane is only 38% monodeuterated. The product of this reaction ($\mathbf{2}_{deut}$) is hydrolyzed with D_2O to produce 2.6 equiv (per Ta) of neopentane as a mixture of neopentane-d_0, -d_1, -d_2, and -d_3 (3.3:54.4:36.7:5.5). The presence of neopentane-d_3 is evidence for the incorporation of deuterium into the tantalum surface complex during the synthesis of **2a/2b**. The volatile product of the reaction of $\mathbf{2}_{deut}$ with acetone is 1 equiv of 2,4,4-trimethyl-2-pentene which is 15% monodeuterated, demonstrating some incorporation of deuterium in the carbenic positions of $\mathbf{2}_{deut}$. The isotopomeric distribution in the volatile products of these reactions is traced to a mechanism of formation of **2a,b** in which the first reaction of surface silanol with **1** is the addition of O–H across the Ta=C double bond.

Introduction

Alkylidene complexes are generally considered to be the reactive intermediates in the metathesis of olefins and in the polymerization of alkynes.[1] The presence of alkylidene species in heterogeneous catalysts for these reactions has often been suggested but rarely confirmed. Such species have been indicated by infrared spectroscopy[2] and by chemical reactivity[3] but the actual surface organometallic species have never been fully characterized.

We report herein that the reaction of $Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_3$ (**1**) with partially dehydroxylated silica produces a mixture of surface tantalum(V) alkylidene complexes formulated $(\equiv SiO)_xTa(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_{3-x}$ ($x = 1, 2$) (**2**). The reaction of **1** with deuterated silica surface SiO–D silanols leads to partially deuterated **2**. Detailed analyses of the isotopomeric distribution of reaction products are compared favorably to a mechanistic model which supposes that alkylidene complexes are formed by a mechanism of initial addition of surface silanol across the tantalum–carbon double bond of **1**, producing a tetraalkyl tantalum siloxide intermediate which then can undergo an elimination of neopentane via α-hydride transfer to form a carbene complex.

Results and Discussion

Reaction Followed *in Situ* by Infrared Spectroscopy. When the tantalum(V) alkylidene complex $Ta[=CHC(CH_3)_3][CH_2C(CH_3)_3]_3$ (**1**)[4] was sublimed onto a disk of silica which has been dehydroxylated at 500 °C ($SiO_{2(500)}$, 20 mg), the infrared spectrum (Figure 1) showed that the band attributed to linear silanol groups[5] at 3747 cm^{-1} (Figure 1a) disappeared totally and instantaneously on contact at room temperature with the tantalum alkylidene complex. At the same time, a group of bands appeared in the regions 3000–2800 and 1500–1300 cm^{-1}, which are attributed to ν(C–H) and δ(C–H) vibrations of neopentyl and/or neopentylidene groups. Excess **1** was removed under vacuum at 80 °C (Figure 1b). The gaseous product of this reaction was identified as neopentane by gas chromatography coupled with mass spectroscopy. The simultaneous decrease in the intensity of surface silanol bands and increase in the intensity of ν(C–H) and δ(C–H) bands, together with the release of neopentane, suggest the formation of one or several chemisorbed organotantalum surface species, **2**.

Characterization of 2: Elemental Analysis. Elemental analysis for tantalum of the silica disk described above was performed and confirmed the presence of tantalum in **2** (5.15% Ta). The reaction was reproduced on a larger scale (500 mg). This allowed for transfer of the tantalum-bearing material under inert atmosphere and thus simultaneous tantalum and carbon analyses. The Ta/SiO_2 material was found to contain 3.04%

[®] Abstract published in *Advance ACS Abstracts,* April 1, 1995.

[1] (a) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cyclo-olefins*; Wiley & Sons: New York, 1985. (b) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983.

[2] (a) Vikulov, K. A.; Elev, I. V.; Shelimov, B. N.; Kazansky, V. B. *Catal. Lett.* **1989**, *2*, 121–124. (b) Shelimov, B. N.; Elev, I. V.; Kazansky, V. B. *J. Mol. Catal.* **1988**, *46*, 187–200.

[3] (a) Weiss, K.; Lössel, G. *Angew. Chem., Int. Ed. Eng.* **1989**, *28*, 62–4. (b) Buffon, R.; Choplin, A.; Leconte, M.; Basset, J.-M.; Touroude, R.; Herrmann, W. A. *J. Mol. Catal.* **1992**, *72*, L7–L10. (c) Buffon, R.; Leconte, M.; Choplin, A.; Basset, J.-M.; *J. Chem. Soc., Chem. Commun.* **1993**, 361–362.

[4] Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370.

[5] (a) Hoffman, P.; Knözinger, E. *Surf. Sci.* **1987**, *188*, 181–198 and references therein. (b) Gillis-d'Hamers, I.; Vrancken, K. C.; Possemiers, K.; Vansant, E. F.; De Roy, G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3091–3093.

0002-7863/95/1517-4288$09.00/0

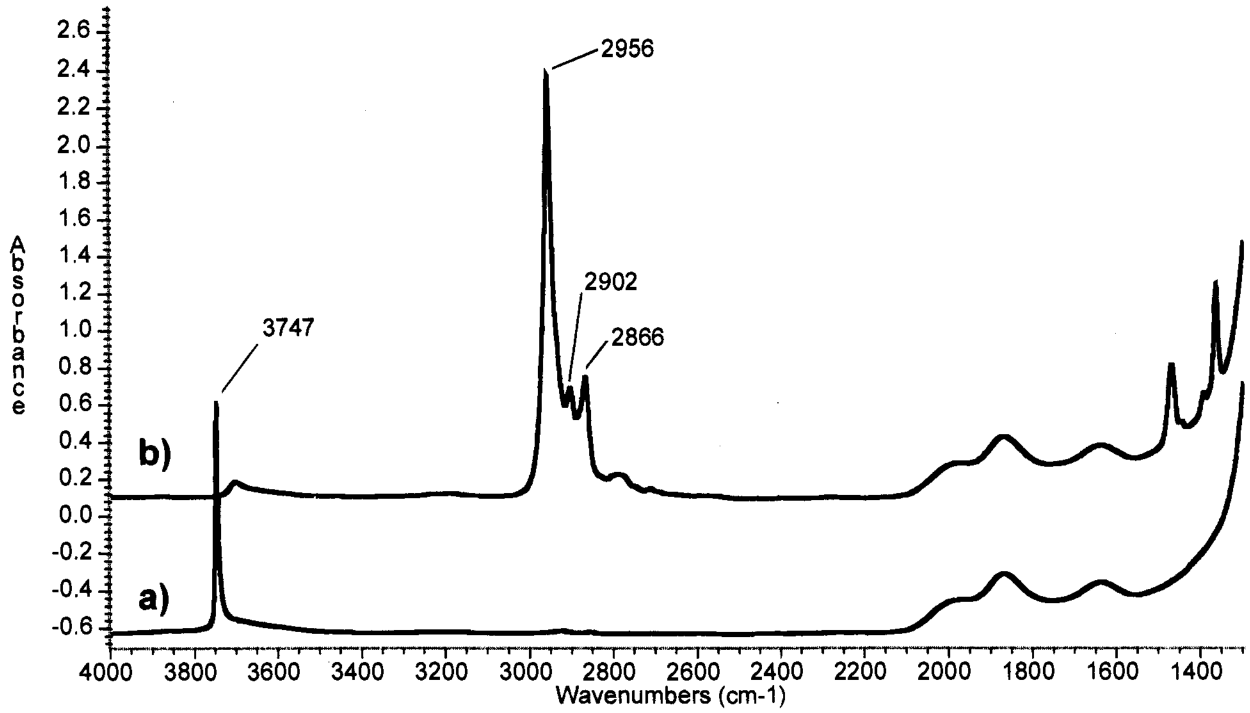


Figure 1.

Ta and 2.18% C. The carbon/tantalum ratio (11.6 C/Ta) indicates that there are, on average, 2.3 C_5 ligands per tantalum center.

Characterization of 2: Confirmation and Quantification of the Neopentane Product. The reaction between **1** and surface silanols was repeated using deuterated silica$_{(500)}$ (>90% Si−OD by IR) on a larger scale (500 mg, 3.37% Ta, 3.0 μmol of Ta). The neopentane given off during the adsorption/desorption process was trapped and quantified (4.1 μmol of C_5H_{12}, 1.35 mol/mol of Ta).[6] Mass spectroscopy indicated a mixture of nondeuterated, monodeuterated, and bisdeuterated neopentane (60.7, 37.8, and 1.5%, respectively). The presence of some deuterated neopentane demonstrates that at least some of the neopentane given off is the result of reaction between tantalum and the surface silanols. At first glance, one might think that the nondeuterated neopentane was an indication of decomposition of the starting material or other intramolecular reactions and dismiss the 1.5% neopentane-d_2 as aberrant, but we shall demonstrate that these values are the result of silanol addition over the Ta=C double bond prior to the α-elimination of neopentane (*vida infra*).

Characterization of 2: Assay of Neopentyl Ligands in 2 and Carbon Balance. The reaction of **2** with D_2O was followed *in situ* by infrared spectroscopy. The silica disk, initially (as **2**) yellow, was exposed to heavy water vapor (15 Torr) and turned white instantly on contact. The infrared spectrum at this stage showed a strong decrease in the intensity of the bands in the region 3000−2500 and 1500−1350 cm^{-1}, which are attributed to ν(C−H) and δ(C−H) vibrations of neopentyl and/or neopentylidene groups. At the same time, there appeared a relatively sharp band at 2783 cm^{-1} assigned to ν(TaO−D) together with the bands associated with isolated and hydrogen-bound silanol ν(SiO−D) bands (2760 cm^{-1} (sharp) and 2730 cm^{-1} (broad)). Although the color change of yellow to white was instantaneous, it was necessary to leave the reaction for 16 h at room temperature to achieve complete disappearence of ν(C−H) and δ(C−H) bands.

The conditions of complete reaction thus established, the deuterolysis was repeated on a larger scale (200 mg) and with **2** produced by the reaction between **1** and deuterated silica$_{(500)}$ (>90% D) ($\mathbf{2}_{deut}$). The gaseous product of the reaction was neopentane (2.6 mol/mol of Ta), and thus, taking into account the 1.35 mol/mol of Ta released during the formation of $\mathbf{2}_{deut}$ (vida supra), all four (3.95 equiv neopentane) C_5 ligands of the starting complex **1** are accounted for. The neopentane produced during deuterolysis was a mixture of neopentane-d_0 (3.3%), -d_1 (54.4%), -d_2 (36.9%), and -d_3 (5.5%). The appearence of neopentane-d_2 and -d_3 confirmed the presence of an alkylidene ligand, and furthermore, the presence of neopentane-d_3 indicated that the complex $\mathbf{2}_{deut}$ was partially deuterated at the carbenic position.

Characterization of 2: CP-MAS ^{13}C NMR. The yellow material, **2**, was transferred under argon into a zirconia drum for CP-MAS ^{13}C NMR analysis. Broad peaks were observed in the NMR spectrum at 33 and 45 ppm.

The solution ^{13}C NMR spectrum of the starting carbene **1** in benzene had four peaks. A peak at 35 ppm was assigned[4] to the methyl groups of neopentyl and neopentylidene groups and the quaternary carbons of the neopentyl groups of **1**. A small peak at 47 ppm was assigned to the quaternary carbon of the *neopentylidene* group. The methylene groups of the neopentyl ligands produced a signal at 117 ppm, and the carbenic carbon of the neopentylidene group appeared at 249 ppm.

The peak observed in the solid state ^{13}C NMR of **2** at 33 ppm is quite similar to that observed by Schrock for **1** (35 ppm, all CH_3 and $CH_2C(CH_3)_3$). More significantly, the presence of a neopentylidene ligand is implied by the peak observed in the solid state ^{13}C NMR of **2** at 45 ppm, that which would correspond to the quaternary carbon of the neopentylidene ligand (47 ppm in **1**). Neither the methylene carbons nor the carbenic carbon was observed, but it is common in solid state NMR that nuclei close to the surface (in this case, directly attached to a grafted metal atom) are not observed. This observation can be attributed to the lack of thermal motion (and thus spin-rotation relaxation) near the surface. Another possible cause of the absence of these peaks could be broadening due to coupling of

---

[6] Based on the elemental analysis of the catalyst obtained after the experiment.

the α-carbons with the tantalum. Nevertheless, we can note that the ^{13}C CP-MAS *NMR* spectrum obtained for **2** is consistent with a surface species similar to **1**.

Characterization of 2: Determination of Surface Carbene. Schrock reported that the pseudo-Wittig reaction between acetone and **1** in pentane solution (25 °C, instantaneous) leads to the formation of 2,4,4-trimethyl-2-pentene (80% yield) and $[O{=}TaNp_3]_n$.[7] Schrock repeated the reaction using the monodeuterated $Ta(=CDC(CH_3)_3)(CH_2C(CH_3)_3)_3$ (deuterated >90% D at the carbenic position). The olefin product was >90% monodeuterated, indicating that in the pseudo-Wittig reaction the acetone reacts exclusively with the carbene ligand.

Assuming that the pseudo-Wittig reaction would be as selective for the surface carbene, as it was for the molecular carbene we expected that the reaction of **2** with acetone vapor would produce 2,4,4-trimethyl-2-pentene. Indeed, the reaction of **2** (3.72% Ta, 15.2 μmol of Ta) with an excess of acetone produced 1 equiv of the olefin (15.6 μmol). This indicates that **2** has, on average, one neopentylidene ligand per tantalum. The reaction of $\mathbf{2}_{\text{deut}}$ with acetone produced 2,4,4-trimethyl-2-pentene (31.9 μmol of Ta produced 34.1 μmol of olefin). Again, 1 mol of olefin/mol of tantalum grafted was produced and was found to be 15% monodeuterated, confirmation that the neopentylidene ligand of **2** was partially deuterated.

Characterization of 2: Summary. Thus we have established by elemental analysis and infrared spectroscopy a reaction between surface silanols and **1** producing a surface tantalum complex bearing hydrocarbyl ligands. From the elemental analysis we established a first estimate of 2.3 C_5 ligands per tantalum center. The formation of **2** was accompanied by the release of neopentane gas (1.35 equiv). The deuterolysis of **2** produced 2.6 equiv of neopentane, accounting for all four C_5 ligands of **1**. These two results suggest that **2** bears 2.6 C_5 ligands. The reaction of **2** with acetone produced 1 equiv of the Wittig-type product 2,4,4-trimethyl-2-pentene, indicating the presence of one carbene ligand per tantalum. On the basis of these results, we suggest that the reaction of surface silanols with **1** leads to silica-supported tantalum complexes connected by one or two siloxy bridges to the surface, $(\equiv SiO)_x Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_{3-x}$ ($x = 1, 2$), **2** (eq 1). In the reaction of **1** with a deuterated silica surface, deuterium from the surface silanol SiO—D is partially incorportated into the surface complex.

$$x{\equiv}SiOH + Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_3 \xrightarrow{RT} (\equiv SiO)_x Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_{3-x} + xC(CH_3)_4 \quad (1)$$

Mechanism of Formation of 2: The Hypothetical Addition of ≡SiO—D across Ta=C. The results of these experiments using silica$_{(500)}$ which had been deuterated (>90% OD) indicated an immediate difference from previous model reactions. Wolczanski[8] and co-workers reported that the reaction between **1** and a frequently used silica model compound, $((CH_3)_3C)_3SiOH$ (siloxH), produces $(silox)Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_2$ and neopentane. The reaction of **1** and siloxD (>90% D) produced $(silox)Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_2$ and exclusively neopentane-d_1 (>90% D).

Our observation of neopentane-d_0 and -d_2 during the reaction of **1** with ≡SiOD and of neopentane-d_3 from the deuterolysis of $\mathbf{2}_{\text{deut}}$ can be explained by a grafting mechanism in which the reaction of **1** with surface silanols takes place by first step addition of the silanol O—H(D) bond across the tantalum−*n*-pentylidene (Ta=C) double bond and not by the direct protolytic cleavage by the silanol of a tantalum−neopentyl (Ta—C) single bond. Precedent for this hypothesis is found in the reported addition of HCl over the (Ta=C) double bond of **1** leading to the product Np_4TaCl.[4]

By applying this mechanism to the reaction of **1** with surface silanols, one can neatly explain the aforementioned mass spectroscopic results. The addition of the first silanol SiO—H over the tantalum carbon double bond leads to an intermediate having four equivalent neopentyl ligands and one siloxy ligand, the silica bulk $(\equiv SiO)Ta(C\mathit{H_2}C(CH_3)_3)_4$, type A (Scheme 1). Elimination of a neopentyl ligand with α-proton abstraction leads to the products, neopentane, and the tantalum surface alkylidene complex $(\equiv SiO)Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_2$ (**2a**). In the reaction of **1** with a deuterated silanol ≡SiO=D, the deuterium in the intermediate (A) occupies one of the eight equivalent methylene positions, $(\equiv SiO)Ta(C\mathit{HD}C(CH_3)_3)(C\mathit{H_2}C(CH_3)_3)_3$. In the product, these eight protons translate into either one of the three methyl protons of the neopentane, $C\mathit{H_3}C(CH_3)_3$, or the alkylidene proton, $(\equiv SiO)Ta(=C\mathit{H}C(CH_3)_3)(CH_2C(CH_3)_3)_2$, or one of the four methylene protons of the two neopentyl ligands, $(\equiv SiO)Ta(=CHC(CH_3)_3)(C\mathit{H_2}C(CH_3)_3)_2$. Thus in the reaction of **1** with deuterated silica, the primary product **2a** is actually a mixture of three isotopomers (Scheme 1, right): nondeuterated (37.5%), deuterated at a methylene position (50%), and deuterated at the alkylidene (12.5%). The neopentane released in the formation of **2a** is 37.5% monodeuterated.

Previous studies[5] have demonstrated the presence of geminal and vicinal silanols on the silica$_{(500)}$ surface. The quantitative analyses of neopentane released during the reaction of **1** and silica$_{(500)}$ (i.e., 1.35 mol of neopentane/Ta) lead us to consider the possibility of the addition of a nearby second ≡SiO—D to the Ta=C double bond to produce an intermediate in which tantalum is bound to the silica surface by two siloxy groups, $(\equiv SiO)_2Ta(CH_2C(CH_3)_3)_3$, type B, which can undergo elimination to produce the surface carbene, $(\equiv SiO)_2Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)$ (**2b**), and a second equivalent of neopentane. By starting from the three isotopomers **2a**, the mechanistic scheme was expanded to include this possibility. Scheme 2 shows this expansion for one of the three isotopomers of **2a**. The relative ratios for the five possible tantulum products and the three isotopomers of the neopentane product of this second step are given in Table 1. Note that since 62.5% of **2a** was monodeuterated (Scheme 1), bisdeuterated neopentane was can also be expected as a product of the second addition/elimination cycle (12.5% of neopentane given off in second cycle).

Mechanism of Formation of 2: Comprehensive Model. The extents of deuteration of silica and heavy water (90% D) are included to produce a general model for the isotopomeric distribution of products of the reaction of **1** with deuterated silica$_{(500)}$. Neopentane products formed with **2** are calculated directly as a function of the **2a**/**2b** ratio. The isotopomeric composition of the surface complexes (**2a**,**b**) are used to predict the distribution of deuterium in the products of the deuterolysis reaction and the Wittig reaction. The possibility of primary kinetic isotope effects is neglected. Such effects would be expected to be miniscule on the basis of the mechanism proposed. Table 2 is a summary of the isotopic distributions of the products of the various reactions studied as a function of the ratio of **2a** to **2b**.

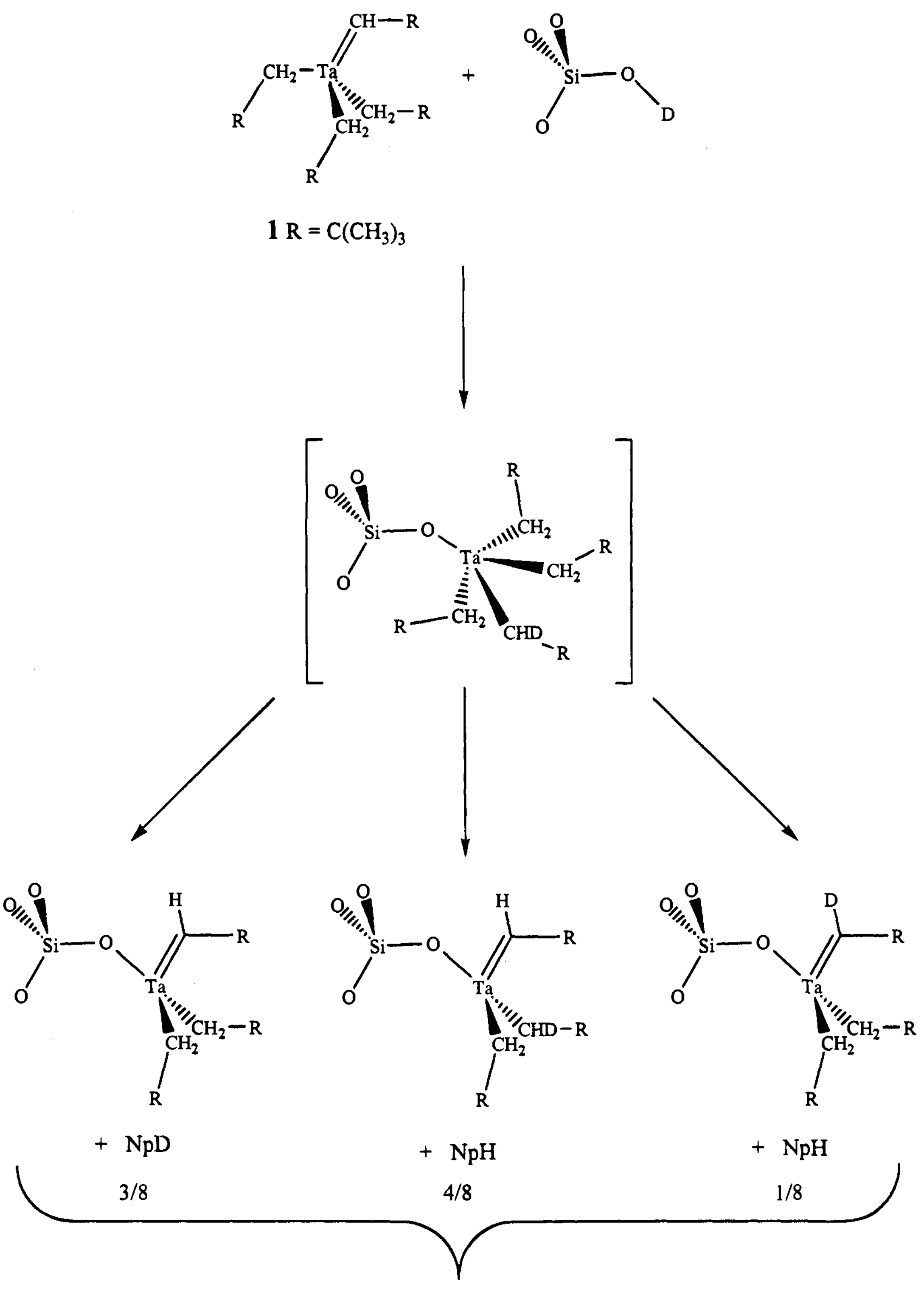
The experimental results are listed on one line in boldface in Table 2. This line is placed in the position coherent with the *quantitative* results, that is the number of moles of neopentane

---

[7] Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399−5400.

[8] LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1985**, *4*, 1810−1818.

Scheme 1



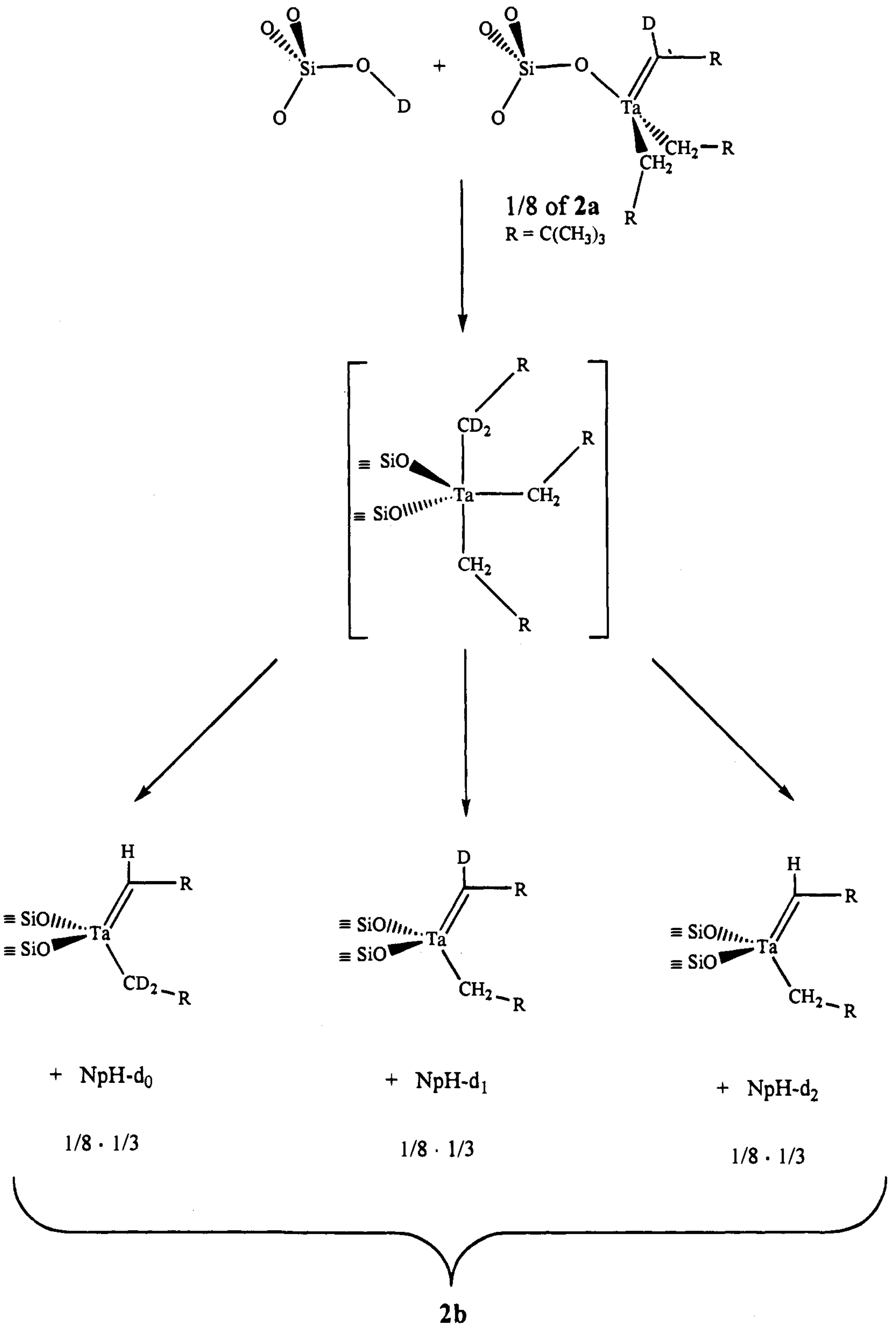
2a

per grafted tantalum given off during the reaction of **1** with silica and during the deuterolysis of **2**. For example, the deuterolysis of **2** produced 1.35 mol of neopentane/mol of Ta grafted. *A priori* this value indicates that the surface species was a mixture of 65% **2a** (producing 0.65 equiv of C_5H_{12}) and 35% **2b** (producing 0.7 equiv of C_5H_{12}, thus a total of 1.35 equiv). In our broader experience with this reaction (i.e., more than 20 experiments but under less rigorously controlled conditions), we have found that the ratio between neopentane released and tantalum adsorbed varies from 1.2 to 1.6:1 with an average value at 1.3:1. The position of the experimental results in Table 2 represents the best estimate of **2a**/**2b** based on quantitative results.

Mechanism of Formation of 2: Comparison of Experiment and Model. The goodness of the fit of this model confirms that the reaction between **1** and silica proceeds by a first step addition of silica surface O−H across the tantalum−carbon double bond and subsequent elimination of neopentane and not by the direct reaction of the neopentyl ligand of **1** with surface O−H.[9]

For the sublimation of **1** onto deuterated (>90% D) silica, for a mixture of 65% **2a** and 35% **2b** (as indicated by the

Scheme 2



quantity of neopentane given off in that particular experiment) we would expect 90% neopentane-d_1 from a direct reaction and 39% neopentane-d_1 from the addition/elimination process. Experimentally, we found 37.8% neopentane-d_1. Additionally, we detected neopentane-d_2 (1.5% of all neopentane), which is unaccounted for by the direct reaction mechanism and predicted to be 3% of total neopentane by the addition/elimination mechanism.

For the deuterolysis of **2** (60% **2a** and 40% **2b**), the direct reaction mechanism predicts that the distribution of neopentane-d_0:-d_1:-d_2:-d_3 would be 7:62:31:0 while the addition/elimination mechanism predicts 5:47:42:6. The experimental distribution was found to be 3.3:54.4:36.7:5.5. Although the overall fit is

---

(9) A third mechanistic model was considered. In this model, addition of SiO—D across the Ta=C bond produces a type A intermediate which, rather than undergoing transfer elimination of neopentane to form **2a**, undergoes protolytic cleavage of a tantalum neopentyl Ta—C bond to form directly a type B intermediate. The experimental results cannot be consistently fitted to such a model.

Table 1. Theoretical Distribution of Deuterium in the Tantalum Products (**2b**) and Neopentane Produced in the Reaction of a Second $\equiv$Si—OD with **2a**

tantalum product (**2b**) and neopentane isotopomers	rel abund
$(\equiv SiO)_2Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)$	15/48
$(\equiv SiO)_2Ta(=CHC(CH_3)_3)(CH\mathbf{D}C(CH_3)_3)$	18/48
$(\equiv SiO)_2Ta(=CHC(CH_3)_3)(C\mathbf{D}_2C(CH_3)_3)$	2/48
$(\equiv SiO)_2Ta(=C\mathbf{D}C(CH_3)_3)(CH_2C(CH_3)_3)$	9/48
$(\equiv SiO)_2Ta(=C\mathbf{D}C(CH_3)_3)(CH\mathbf{D}C(CH_3)_3)$	4/48
$C(CH_3)_4$	12/48
$\mathbf{D}CH_2C(CH_3)_3$	30/48
$\mathbf{D}_2CHC(CH_3)_3$	6/48

Table 2. Expected Isotopomeric Distribution[a] of the Gaseous Products of Various Reactions Together with the Experimental Results (in Boldface)

		sublimation[b]				deuterolysis[c]					pseudo-Wittig[d]	
%**2a**	%**2b**	d_0	d_1	d_2	eq[e]	d_0	d_1	d_2	d_3	eq[e]	d_0	d_1
100	0	66	34	0	1.00	6	53	38	3	3.00	89	11
95	5	65	35	1	1.05	5	53	39	3	2.95	88	12
90	10	64	36	1	1.10	5	52	39	4	2.90	87	13
85	15	62	36	1	1.15	5	51	40	4	2.85	87	13
80	20	61	37	2	1.20	5	51	40	4	2.80	86	14
75	25	60	38	2	1.25	5	50	41	5	2.75	85	15
70	30	60	38	2	1.30	5	49	41	5	2.70	85	15
		60.7	**37.8**	**1.5**	**1.35**	**3.3**	**54.4**	**36.9**	**5.5**	**2.60**	**85**	**15**
65	35	59	39	3	1.35	5	48	42	5	2.65	84	16
60	40	58	39	3	1.40	5	47	42	6	2.60	84	16
55	45	57	40	3	1.45	5	46	43	6	2.55	83	17
50	50	57	40	3	1.50	5	46	44	6	2.50	82	18
45	55	56	41	4	1.55	4	45	44	7	2.45	82	18
40	60	55	41	4	1.60	4	44	45	7	2.40	81	19
35	65	55	41	4	1.65	4	42	46	8	2.35	80	20
30	70	54	42	4	1.70	4	41	47	8	2.30	80	20
25	75	54	42	4	1.75	4	40	47	9	2.25	79	21
20	80	53	42	5	1.80	4	39	48	9	2.20	78	22
15	85	53	43	5	1.85	4	38	49	10	2.15	78	22
10	90	52	43	5	1.90	3	36	50	10	2.10	77	23
5	95	52	43	5	1.95	3	35	51	11	2.05	76	24
0	100	52	43	5	2.00	3	34	52	11	2.00	76	24

[a] Si—OD/Si—OH = 9:1. [b] Neopentane from [**1** + $\equiv$SiOD → **2** + $C(CH_3)_4$-d_x]. [c] Neopentane from [**2** + D_2O → $[Ta]_s(=O)_y(OD)_z$ + $C(CH_3)_4$-d_x]. [d] 2,4,4-Trimethyl-2-pentene from [**2** + $(CH_3)_2CO$ → $(CH_3)_2C{=}CHC(CH_3)_3$-d_x + $[Ta]_s{=}O$]. [e] Equivalents with respect to grafted tantalum.

not as decisive for this experiment as it was for the sublimation, the presence of neopentane-d_3 cannot be accounted for by the direct reaction model.

The reaction of **2** with acetone is expected to produce exactly 1 equiv of 2,2,4-trimethyl-2-pentene regardless of the ratio **2a**/**2b**. The addition/elimination model predicted that the reaction of **2** with acetone would produce significant (11−24%) amounts of deuterated olefin product, regardless of the **2a**/**2b** ratio. The direct reaction mechanism for the formation of **2** does not predict deuterium incorporation into the olefin. Experimentally we found that the olefin was 15% deuterated, which is consistent with a mixture of 70% **2a** and 30% **2b**.

Conclusions

The reaction of **1** with a partially dehydroxylated silica leads to formation of a mixture of surface alkylidene complexes, $(\equiv SiO)Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_2$ (**2a**, 65 ± 10%) and $(\equiv SiO)_2Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)$ (**2b**, 35 ± 10%). The reaction proceeds by first step addition of surface silanol (O—H) across the tantalum−carbon (Ta=C) double bond followed by later elimination of neopentane, producing one carbene ligand per tantalum center.

Further studies are underway concerning the reactivity of **2**, in particular its reactivity with hydrogen.

Experimental Section

General Procedure. All manipulations and reactions were conducted in the absence of solvent under strict inert atmosphere or vacuum conditions. Sealed tube reactors were used throughout. The extremely air and water sensitive surface-supported tantalum complexes were stored in sealed pyrex break-seal tubes apt for the construction of secondary reactors (for the chemical assays of the surface complex). **2** showed no evidence of decomposition when stored for a period of 2 weeks at −40 °C in such tubes. Infrared spectra were recorded on a Nicolet 10MX-FT spectrometer equipped with a cell designed for *in situ* preparations under controlled atmosphere.[10] Gas phase analysis was performed on a Intersmat IGC 121 FL equipped with a flame ionization detector and a Al_2O_3/KCl on a fused silica column (50 m × 0.32 mm). Elemental analyses were performed by the Central Analysis Service of the CNRS at Solaize and (for inert atmosphere determination of carbon and tantalum in **2**) Mikroanalytisches Labor Pascher, Remagen, Germany. Mass spectra were recorded on a quadrupole analyzer (Supravac VG) connected to a vacuum system able to maintain a residual pressure of 10^{-10} Torr.

Silica (Degussa, 200 m^2/g) was treated under vacuum (10^{-5} mmHg) at 500 °C for 15 h. Silica thus treated has been determined to have surface hydroxyl concentration of 2 OH/nm^2 as determined by the titration with $LiAlH_4$.[11] Deuterated silica was prepared by heating normal silica$_{(500)}$ under D_2O (>90% D, 22 mmHg) at 500 °C for 3−4 h followed by evacuation at that temperature for 3−4 h. This procedure was repeated three times before a final dehydroxylation at 500 °C for 15 h. The acetone (Prolabo, Normapur) was distilled over $CaCl_2$, degassed, and stored over molecular sieves (4 A). D_2O (Aldrich) was degassed and stored under vacuum. **1** was prepared by the method of Schrock.[4]

Preparation of $(\equiv SiO)_xTa(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_{3-x}$ (x = 1, 2), (2). $Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_3$ was sublimed under vacuum (10^{-5} mmHg) at 80 °C onto the silica$_{(500)}$. The silica takes on a yellowish color. Unreacted starting material was removed by sublimation under vacuum for 2 h at the same temperature. Gases were trapped in a liquid nitrogen cooled tube and sealed for later analysis. Air was admitted to this trap to atmospheric pressure just before GC/MS analysis.

MAS NMR spectroscopy. MAS NMR spectra were recorded on a BRUKER MSL-300 spectrometer operating at 75.47 MHz for ^{13}C. The probehead was a commercial double-tuned 7 mm double-bearing system from BRUKER allowing spinning frequencies up to 4 kHz. The samples were introduced in the rotor made of zirconia under a dry nitrogen atmosphere in a glovebox and tightly closed. Boil-off nitrogen was used for both bearing and driving the rotors. For ^{13}C NMR, a typical cross-polarization sequence was used: 90° rotation of the ^{1}H magnetization (impulsion length 6.2 μs), then contact between carbon and proton during T_C = 5 ms, and finally recording of the spectrum under high-power decoupling. The delay between each scan was fixed to 5 s, to allow for the complete relaxation of the ^{1}H nuclei. Chemical shifts are given with respect to TMS by using adamantane as an external reference (δ = 37.7 ppm for the highest chemical shift).

Reaction of 2 (or 2_{deut}) with D_2O. The D_2O was vacuum distilled into a reactor containing **2**. The solid turned from yellow to white immediately on contact with the water vapor. Infrared spectra indicate that the reaction was complete within 15 h at room temperature. Gases released were transferred *in vacuo* into a trap cooled by liquid nitrogen and sealed. Air was admitted to this trap to atmospheric pressure just before GC/MS analysis.

Reaction of 2 (or 2_{deut}) with Acetone. A reactor containing **2** (or 2_{deut}) was filled with acetone vapor (excess with respect to tantalum) at room temperature. The solid turns from yellow to beige instantaneously. Nevertheless **2** was left in contact with acetone for 2 h to insure complete reaction. 2,4,4-Trimethyl-2-pentene was transferred *in vacuo* into a trap equipped with a septum and cooled by liquid

---

(10) Psaro. R.; Ugo. R.; Zanderighi, G. M.; Besson, B.; Smith, A. K.; Basset, J.-M. *J. Organomet. Chem.* **1981**, *213*, 215−247.

(11) Silica characteristics are provided by DEGUSSA (technical note).

nitrogen and then sealed. To this was syringed heptane (~3 μL) as an internal standard and hexane as a solvent (~3 mL). The liquid was then analyzed by GC/MS.

Acknowledgment. The authors wish to thank Robert Bacaud of the Institut de Recherche sur la Catalyse, Villeurbanne, for mass spectral analysis. The financial support of Amoco is gratefully acknowledged. The authors also wish to thank the French Ministry of Foreign Affairs for a *Bourse Chateaubriand* (G.P.N.).

Supplementary Material Available: ^{13}C NMR spectra of **1** and **2** and a detailed description of the model used to calculate the isotopomeric distribution of product **2** as a function of the relative amounts of **2a** and **2b** including full reaction schemes, computer program, and output (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9411560