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High-Resolution Solid-State ^{13}C NMR Studies of Chemisorbed Organometallics. Chemisorptive Formation of Cation-like and Alkylidene Organotantalum Complexes on High Surface Area Inorganic Oxides

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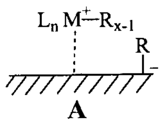
Abstract: ^{13}C CPMAS NMR spectroscopy has been employed to investigate the surface chemistry of the organotantalum hydrocarbyl/alkylidene complexes, $Cp'Ta(^{13}CH_3)_4$ (**1***), $Cp_2Ta(^{13}CH_3)_3$ (**2***), $Cp_2Ta(^{13}CH_2)(^{13}CH_3)$ (**3***), and $Ta(^{13}CH^tBu)(^{13}CH_2{}^tBu)_3$ (**4***) [$Cp' = \eta^5$-$(CH_3)_5C_5$, $Cp = \eta^5$-C_5H_5] supported on partially dehydroxylated silica (PDS), dehydroxylated silica (DS), or dehydroxylated γ-alumina (DA). Mono-Cp tantalum hydrocarbyl **1*** undergoes chemisorption to form $Cp'Ta(^{13}CH_3)_3O$-Si μ-oxo species on silica, and “cation-like” $Cp'Ta(^{13}CH_3)_3^+$ and $Cp'Ta(^{13}CH_3)_3O$-Al μ-oxo species on DA, via pathways analogous to those established for organo-group 4 and actinide complexes. When supported on DA, bis-Cp tantalum hydrocarbyl **2*** follows the same chemisorption mode as **1***. However, when **2*** is chemisorbed on PDS and DS, a “cation-like” $Cp_2Ta(^{13}CH_3)_2^+$ species is the major adsorbate product. On PDS, bis-Cp tantalum alkylidene complex **3*** is converted predominantly to a stable “cation-like” $Cp_2Ta(^{13}CH_3)_2^+$ species, presumably via electrophilic addition of a proton from the PDS surface. In contrast to **3***, Ta alkylidene complex **4*** forms predominantly a $Ta(^{13}CH^tBu)(^{13}CH_2{}^tBu)_2O$-Si, μ-oxo-alkylidene species on PDS.

Introduction

Chemisorptive interactions of metal-organic complexes with oxide surfaces and the hydrocarbon transformation activities of the resulting adsorbate molecules have been of great recent interest.[1] Accompanying recent advances in single-site olefin polymerization catalysis,[2] the chemisorption reactions of group 4 and related metal hydrocarbyls with high surface area inorganic supports have been the subject of intense research effort due to their importance in large-scale polymerization processes[3] and the possibility of fine-tuning catalytic properties at the molecular level.[2] Structural characterization, which for homogeneous catalysts is almost universally and straightforwardly achieved by spectroscopic and/or X-ray crystallographic techniques,[2] is likewise essential in understanding such surface organometallic chemistry and in controlling the nature and modes of chemisorptive reactions between organometallic molecules and inorganic surface functionalities, hence to manipulate catalytic pathways. Our previous spectroscopic and catalytic studies of organo-group 4 and actinide complexes supported on high surface area metal oxides and halides revealed that highly electrophilic “cation-like” species (**A**) are formed on Lewis acidic surfaces[4] such as dehydroxylated γ-alumina (DA; ca. 0.12 $OH_{surface}/nm^2$) and $MgCl_2$ via the transfer of an alkyl ligand from the metal center to a coordinatively unsaturated



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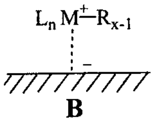

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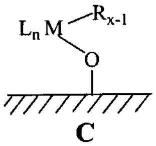

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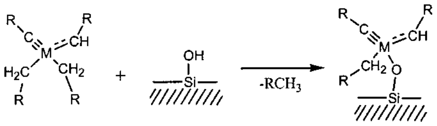
surface Lewis acid site. Also, on very strongly Brønsted acidic surfaces (the conjugate base sites of which are weak Brønsted bases) such as sulfated zirconia, similar cationic species (**B**) are formed via protonolytic cleavage of an alkyl ligand.[5] Both pathways have close analogues in solution phase chemistry.[2c] On the other hand, on weak Brønsted acidic surfaces (having strong conjugate base sites)[4b,6] such as partially dehydroxylated silica (PDS) and MgO, catalytically inert "μ-oxo-like" adsorbate structures (**C**) are formed exclusively via protonolysis of an alkyl ligand by a surface hydroxyl group.[7]

While many mid- and late-transition metal hydrocarbyl or alkylidene complexes chemisorbed on inorganic oxides have been reported to be active for various hydrocarbon transformations such as hydrogenation,[8] olefin polymerization,[9] and σ-bond[10]/olefin[11] metathesis, the poorly understood interaction modes of the chemisorbed complexes with the supports are still the subject of speculation and intensive research.[12−14] Metal alkylidene complexes present a particularly interesting case due to their largely unknown reaction mode(s) with surface functionalities, despite their frequently reported catalytic behavior.[9a,10b−d,11a,e] It was only recently that silica-supported Re alkylidene, alkylidyne,[11a] and Mo alkylidyne[15] complexes were structurally characterized by solid-state NMR techniques which showed that μ-oxo alkylidene, alkylidyne species are exclusively formed via protonolysis pathways (e.g., eq 1).



(M = Re, Mo) (1)

Organotantalum precursors should be particularly instructive from the following standpoint: (a) a variety of molecular structures and well-characterized reactive hydrocarbyl/alkylidene functionalities is available,[16] (b) the catalytic activities of the various supported complexes are generally well-defined,[8g,10b−d] and (c) they will serve as model adsorbates "to bridge" the gap between the relatively well-characterized surface chemistry of early organotransition metal complexes and the relatively unexplored chemistry of mid- and late-organotransition metal complexes.

In this report, we investigate the diverse chemisorptive reaction modes, including formation of "cationic" and "alkylidene" adsorbates, of tantalum hydrocarbyl and alkylidene complexes on high surface area Brønsted and Lewis acidic inorganic oxides (e.g., silica, γ-alumina) via ^{13}C CPMAS NMR spectroscopy with isotopic labeling. Spectral parameters and reaction modes are assigned by reference to those of model group 5 compounds and related organo-group 4 and actinide complexes.

Experimental Section

Physical Methods and Synthesis. All synthetic procedures were performed in Schlenk-type glassware interfaced to a high-vacuum line (10^{-5}−10^{-6} Torr) or in a nitrogen-filled Vacuum Atmospheres glovebox (0.5−1.0 ppm O_2). The physical analysis instruments used were ^1H, ^{13}C NMR (Varian Mercury 400 and Varian INOVA 500), ^{13}C CPMAS solid-state NMR (Varian VXR300), BET/pore size distribution (Omnisorb 360), and GC/MSD (Hewlett-Packard 6890). Argon (Matheson) was purified by passage through MnO/vermiculite and Davison 4A molecular sieve columns. All solvents were distilled from Na/K alloy and stored in vacuo in bulbs on the high-vacuum line. Dehydroxylated alumina (DA, American Cyanamid γ-alumina, 99.99% purity) was prepared as previously described.[4c,d,17] Partially dehydroxylated silica (PDS) was prepared by heating Davidson grade 62 silica gel (60−80 mesh, previously washed with 0.1 M HNO_3, and dried) at 450 °C for 12 h under high vacuum (5×10^{-6} Torr). Highly dehydroxylated silica (DS) was prepared from Davidson grade 62 silica gel (60−80 mesh, previously washed with 0.1 M HNO_3, and dried) by calcining it in a stream of CO (flow rate = 100 mL/min) at 950 °C for 1 h, calcining it in a stream of Ar (flow rate = 100 mL/min) at 950 °C, and finally heating it under high vacuum (5×10^{-6} Torr) at 800 °C for 15 h. All synthesized supports were stored under dry N_2 in storage tubes until used. The labeled organotantalum complexes, $Cp'Ta(^{13}CH_3)_4$ (**1***),[18] $Cp_2Ta(^{13}CH_3)_3$ (**2***),[19] and $Cp_2Ta(^{13}CH_2)(^{13}CH_3)$ (**3***)[19] ($Cp' = \eta^5$- $C_5(CH_3)_5$, $Cp = \eta^5$-C_5H_5; all ^{13}C enriched to 99%), were synthesized using $^{13}CH_3I$ (99%, ^{13}C, Cambridge Isotopes) according to the published procedures for the unlabeled analogues.

Synthesis of $Ta(^{13}CH^tBu)(^{13}CH_2{}^tBu)_3$ (4*). A flask of $^{13}CO_2$ (1.0 L, 1.0 atm, 44.6 mmol) equipped with a break-seal and an extra outer J-Young valve was attached to a high-vacuum line. A flask containing ^tBuMgCl (25 mL of a 2.0 M solution in ether, 50.0 mmol) was also attached to the high-vacuum line and evacuated at −78 °C. The reaction

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was initiated and performed in an enclosed volume of the vacuum line by using a magnet to break the break-seal with a magnetic stirring bar, and the $^{13}CO_2$ was introduced to the chilled stirring solution of ^tBuMgCl. The solution was stirred at −15 °C for 12 h, and then 30 mL of distilled water and 7.0 mL of concentrated HCl were carefully syringed in at −20 °C. Two layers formed, and the ether layer was separated, while the water layer was extracted with 3 × 20 mL ether. After drying the combined ether solutions over $MgSO_4$ and filtration, the ether was removed on a rotary evaporator at 0 °C. The resulting $^tBu^{13}CO_2H$ (yield, 92%) was reduced with $LiAlH_4$ in ether to give $^tBu^{13}CH_2OH$ (yield, 95%). Next, the $^tBu^{13}CH_2OH$ was refluxed with Ph_3PCl_2 in DMF to afford $^tBu^{13}CH_2Cl$ (yield, 61%). On the basis of the literature procedure,[20] $Ta(^{13}CH^tBu)(^{13}CH_2{}^tBu)_3$ (**4***) was prepared from $TaCl_5$ and $^tBu^{13}CH_2MgCl$ in turn prepared from $^tBu^{13}CH_2Cl$, and the final organotantalum product was purified by vacuum sublimation.

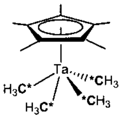
Chemisorption of Organometallic Complexes on Various Synthetic Supports. The samples for ^{13}C CPMAS NMR were prepared on a high-vacuum line. Thus, 10 mL of toluene was condensed onto well-mixed, measured quantities (0.013−0.035 mmol) of the organometallic precursor complex and support (150−200 mg) in a two-sided fritted reaction vessel interfaced to a high-vacuum line. The resulting slurry was next stirred for 1.0 h and filtered. The impregnated support was collected on the frit, washed three times with toluene, and finally dried in vacuo for 3 h. The resulting adsorbate sample was immediately loaded into a solid-state NMR rotor in the glovebox and analyzed by ^{13}C CPMAS NMR spectroscopy.

High-Resolution Solid-State ^{13}C NMR Spectroscopy. ^{13}C CPMAS solid-state NMR spectra were recorded on a Varian VXR300 spectrometer operating at 75.4 MHz (^{13}C). ^{1}H decoupling (ca. 65 kHz), cross-polarization (CP), and magic-angle-spinning, which was calibrated with a neat KBr sample, were employed for routine experiments. The air-sensitive samples were loaded into cylindrical silicon nitride rotors in the glovebox with O-ring sealed Kel-F caps. Because the samples are extremely air- and moisture-sensitive, rotors were loaded and packed with support-adsorbate samples inside the glovebox under a nitrogen atmosphere. Typically, a spinning rate of 6.3 kHz could be achieved with a Doty Scientific 5 mm supersonic probe using boil-off nitrogen as the spinning gas to prevent sample exposure to air. For routine spectra of supported tantalum complexes, the optimum cross-polarization contact time was found to be 2.6−2.7 ms. The optimum recycle time was found to be 4 s. The ^{13}C 90° pulse width and the Hartmann−Hann condition were determined by a parameter-arrayed experiment for each measurement. All solid-state ^{13}C NMR spectra were externally referenced to adamantane by assigning its major peak at δ 37.7. In general, 7500−14 000 scans were required to achieve satisfactory signal-to-noise ratios of the supported organometallic samples. When the coverage of the supported complexes was low and the resonances from Kel-F caps overlapped with sample spectra, sample spectra were obtained by digitally subtracting the Kel-F background spectrum.

Results and Discussion

We begin with the syntheses and general descriptions of labeled organotantalum adsorbates and supports (DA, DS, and PDS). Next, the structural analysis by ^{13}C CPMAS NMR spectroscopy of mono-Cp hydrocarbyl complex, $Cp'Ta(^{13}CH_3)_4$ (**1***), chemisorbed on PDS and DA, is correlated with previous results using organo-group 4 and actinide hydrocarbyls on PDS and DA. We then discuss the spectroscopy of bis-Cp hydrocarbyl complex $Cp_2Ta(^{13}CH_3)_3$ (**2***) supported on DA, DS, and PDS vis-à-vis supported **1*** and the relevant supported organo-group 4 and actinide complexes, followed by analysis of bis-Cp alkylidene complex $Cp_2Ta(^{13}CH_2)(^{13}CH_3)$ (**3***) supported on PDS. Finally, we employ the labeled hydrocarbyl alkylidene complex, $Ta(^{13}CH^tBu)(^{13}CH_2{}^tBu)_3$ (**4***), and analyze the surface chemistry on PDS.

A. Preparation of Adsorbates and Supports. Organotantalum hydrocarbyl/alkylidene complexes having various supporting ligand types and reactive functionalities, viz., mono-Cp hydrocarbyl complex $Cp'Ta(^{13}CH_3)_4$ (**1***), bis-Cp hydrocarbyl complex $Cp_2Ta(^{13}CH_3)_3$ (**2***), bis-Cp alkylidene complex $Cp_2Ta(^{13}CH_2)(^{13}CH_3)_3$ (**3***), and non-Cp alkylidene complex $Ta(^{13}CH^tBu)(^{13}CH_2tBu)_3$ (**4***), are selectively employed as probes of possible chemisorptive reaction pathways. The ^{13}C labeled organotantalum adsorbates, **1***, **2***, and **3***, employed in this study were straightforwardly prepared as described elsewhere for the unlabeled analogues.[18,19] The α-^{13}C enriched complex **4*** was prepared via $^tBu^{13}CH_2Cl$[21] which required a three-step synthesis (eqs 2, 3), followed by subsequent reaction of $TaCl_5$ and with the Grignard reagent prepared from $^tBu^{13}CH_2Cl$ (eq 4).[20]



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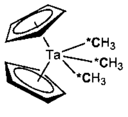

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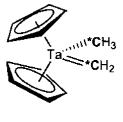

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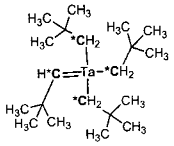

4*

(*C = 99% enriched ^{13}C)

$$^tBuMgCl + {}^{13}CO_2 \xrightarrow[\text{(ii) H}^+\text{, H}_2\text{O}]{\text{(i) ether, }-15\ ^\circ\text{C}} {}^tBu^{13}CO_2H \qquad (2)$$

$$^tBu^{13}CO_2H \xrightarrow[\text{LAH}]{\text{ether}} {}^tBu^{13}CH_2OH \xrightarrow[\text{Ph}_3\text{PCl}_2]{\text{DMF, reflux}} {}^tBu^{13}CH_2Cl \qquad (3)$$

$$^tBu^{13}CH_2Cl \xrightarrow{\text{Mg}} {}^tBu^{13}CH_2MgCl$$

$$TaCl_5 + {}^tBu^{13}CH_2MgCl \xrightarrow[\text{ether}]{} \underset{\mathbf{4^*}}{Ta(^{13}CH^tBu)(^{13}CH_2{}^tBu)_3} \qquad (4)$$

The dehydroxylated alumina employed (DA, American Cyanamid γ-alumina) has a surface area of ~95 m^2/g of by BET measurement and a ca. 6.7 nm most frequent pore radius by the N_2 desorption method. Although the surface is mainly composed of O^{2-} (Lewis base site) and Al^{3+} (Lewis acid site) functionalities, it also contains ca. 0.12 residual OH per nm^2.[3b,17] The BET surface areas of the present partially dehydroxylated silica (PDS, Davidson 62) and highly dehydroxylated silica (DS) are found to be $\gtrsim$250 m^2/g. Surface hydroxyl coverages (determined titrametrically with lithium or Grignard reagents) of ~2 residual OH groups per nm^2 for PDS[22] and 0.4 residual OH per nm^2 for DS have been reported.[22] Moreover, the structures/environments of OH groups, which are suggested on the basis of vibrational spectroscopy, are heterogeneous in character and composed of various populations of geminal, vicinal, and isolated OH groups.[3b]

B. High-Resolution Solid-State ^{13}C NMR Spectroscopy Studies. The ^{13}C solution and solid-state CPMAS NMR spectral parameters of neat and supported tantalum complexes **1***, **2***, **3***, and **4*** are summarized in Table 1. The spectrum of **1***/

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Table 1. Solution Phase and Adsorbate ^{13}C NMR Chemical Shift Data for Tantalum Complexes and Assignments[a]

complex	Cp-ring	Cp′–CH$_3$	Ta–C$_\alpha$	others
Cp′Ta(^{13}CH$_3$)$_4$ (**1***)[b]	119.1	11.9	74.1	
1*/PDS[c]	118	9	59.0	−6 (Si−CH$_3$)
1*/DA[d]	123	11.5	72, 60	−8 (Al−CH$_3$)
Cp$_2$Ta(^{13}CH$_3$)$_3$ (**2***)[b]	104.8		21.6	
2*/DA	113		53, 20	−14 (Al−CH$_3$)
2*/DS[e]	112		58, 15(w)	−9 (Si−CH$_3$)
2*/PDS	113		58, 18(w)	
Cp$_2$Ta(^{13}CH$_2$)(^{13}CH$_3$)[b] (**3***)	100.5		229.3 (Ta═CH$_2$) −3.2 (Ta−CH$_3$)	
3*[f]	102.0		225.7 (Ta═CH$_2$) −2.55 (Ta−CH$_2$)	
3*/PDS	113		57, 18(w)	
Ta(^{13}CH$_2$^{t}Bu)$_3$(^{13}CH^{t}Bu) (**4***)[b]			250.3 (Ta═CHR) 114.1 (Ta−CH$_2$R)	47.0 (CH^{t}Bu,C$_\beta$) 35.3 (CH$_2$^{t}Bu,C$_\beta$) 35.2 (CH$_2$^{t}Bu,C$_\gamma$) 35.0 (CH^{t}Bu,C$_\gamma$)
4*/PDS			247.0 (Ta═CHR) 120.7 (Ta−CH$_2$R) 95.1 (Ta−CH$_2$R)	33.9 (CH$_2$^{t}Bu,C$_\gamma$) 32.0 (CH^{t}Bu,C$_\beta$)

[a] In ppm downfield from Me$_4$Si. [b] Measured in C$_6$D$_6$ solution. [c] Partially dehydroxylated silica. [d] Dehydroxylated alumina. [e] Dehydroxylated silica. [f] Measured as a neat solid (^{13}C CPMAS spectrum).

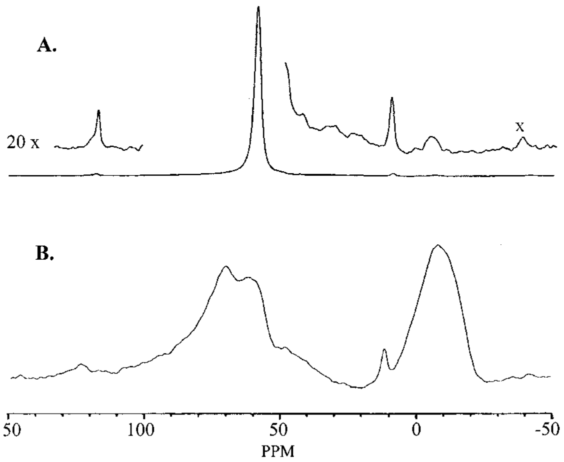
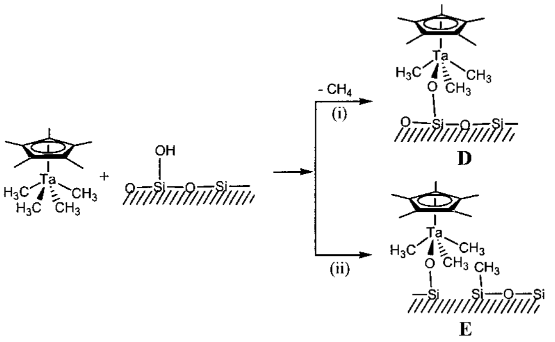


Figure 1. ^{31}C CPMAS NMR spectra of (A) Cp′Ta(^{13}CH$_3$)$_4$ (**1***)/PDS (7500 scans, repetition time = 4 s, contact time = 2.7 ms, spinning speed = 7.5 kHz). (B) Cp′Ta(^{13}CH$_3$)$_4$ (**1***)/DA (11 250 scans, repetition time = 4 s, contact time = 2.7 ms, spinning speed = 7.6 kHz) (x = spinning sideband).

PDS is shown in Figure 1A.[23] By analogy with the ^{13}C NMR data for neat complex **1*** (Table 1), the band at δ 118 is readily assigned to the Me$_5$C$_5$ ring carbon atoms and that at δ 9 to the methyl carbon atoms of Me$_5$C$_5$, respectively. Note that a substantial displacement of the Ta−^{13}CH$_3$ resonance to higher field is observed, δ 59 from δ 74 of **1***. A Cp′Ta(CH$_3$)$_3$OSi≡, μ-oxo species (structure **D**) is reasonably suggested on the basis of the δ(CH$_3$) high-field shift observed in Cp′Ta(CH$_3$)$_3$OR model compounds (δ 52.46, 54.97 for Cp′Ta(CH$_3$)$_3$(OMe),[24] δ 53.94, 49.91 for Cp′Ta(CH$_3$)$_3$(OCHMe$_2$),[24] δ 55.62, 53.96 for [Cp′Ta(CH$_3$)$_3$]$_2$O[25]) and observed methane evolution (δ 0.15 in C$_6$D$_6$) for in situ observed **1** + PDS NMR-scale slurry reactions. Such high-field displacements of the Ta−^{13}**C**H$_3$ chemical shifts may reflect π-donation from the oxo ligand toward the metal center as analogously argued for the cases of organo-group 4 and actinide alkoxides (eq 5).[4−6] A small signal

$$\mathrm{M{-}\ddot{\underset{..}{O}}R} \longleftrightarrow \mathrm{\overset{-}{M}{=}\overset{+}{\underset{..}{O}}R} \qquad (5)$$

at δ −6 in **1***/PDS is assigned to a surface Si-**C**H$_3$ functionality in close analogy to the Si−**C**H$_3$ signal assigned at δ −5.4 for Cp′$_2$Th(CH$_3$)$_2$/DS.[6] Therefore, two concurrent chemisorptive reaction pathways for complex **1** on silica are reasonably suggested (eq 6): (i) Ta−C σ-bond protonolysis by surface silanol groups (structure **D**), which has ample precedent in solution phase organotantalum chemistry,[12,26] and (ii) Ta−C σ-bond addition across surface Si−O bonds to yield a μ-oxo adsorbate, [4b] Cp′Ta(CH$_3$)$_2$−SiO≡, and a Si−CH$_3$ species (Structure **E**). Similar Si−O cleavage reactions have been reported for the surface chemistry of organolithium reagents[6] as well as for group 4 and actinide metal complexes on DS.[4b]



(6)

In contrast to chemisorption on PDS, the ^{13}C CPMAS spectrum of **1***/DA differs markedly from that of **1***/PDS as shown in Figure 1B, and is consistent with previous organo-group 4 and actinide chemisorption results.[4] The labeled Ta−^{13}CH$_3$ signal at δ 60 is reasonably assigned to a μ-oxo Cp′Ta(CH$_3$)$_3$O− species (analogous to structure **D**) on the basis

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(23) (a) In this spectrum, the labeled methyl signal is more intense than the other bands. However, under cross-polarization conditions, relative spectral intensities of individual ^{13}C nuclei cannot be quantitatively correlated due to differential cross-polarization rates and differential decays of the magnetization.[23b,c] (b) Walter, T. H.; Frauenhoff, G. R.; Shapley, J. R.; Oldfield, E. *Inorg. Chem.* **1991**, *30*, 4732−4739. (c) Fyfe, C. A. *Solid-State NMR for Chemists*; CRC Press: Guelph, 1983; Chapters 6 and 7.

(24) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem Soc.* **1983**, *105*, 2651−2660.

(25) Jernakoff, P.; de Bellefon, C. M.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 1362−1364.

(26) (a) Fandos, R.; Hernández, C.; López-Solera, I.; Otero, A.; Rodríguez, A.; Ruiz, M. J. *Organometallics* **2000**, *19*, 5318−5324. (b) LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1985**, *4*, 1810−1818.

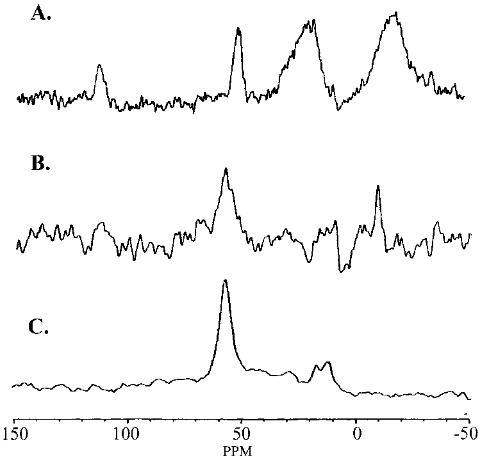
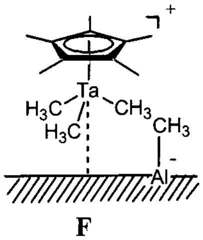
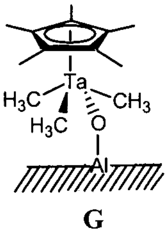


Figure 2. ^{13}C CPMAS NMR spectra of (A) $Cp_2Ta(^{13}CH_3)_3$ (**2***)/DA (12 000 scans, repetition time = 4 s, contact time = 2.6 ms, spinning speed = 6.4 kHz). (B) $Cp_2Ta(^{13}CH_3)_3$ (**2***)/DS (14 000 scans, repetition time = 4 s, contact time = 2.6 ms, spinning speed = 5.1 kHz). (C) $Cp_2Ta(^{13}CH_3)_3$ (**2***)/PDS (12 000 scans, repetition time = 4 s, contact time = 2.6 ms, spinning speed = 6.2 kHz).

of the above results with **1***/PDS. An intense, broad upfield signal at δ −8 is also conspicuous, which is far above the range generally observed for Ta−CH_3 moieties.[18,19,24,25] Noticeably, the signal at this field position with this breath is virtually identical to those of metallocene dimethyls supported on DA.[4c] Here it is argued that the broadening arises from scalar interactions and $^{13}C-^{27}Al$ (^{27}Al: $I = {}^{5}/_{2}$, $Q = 0.149e \times 10^{-24}$ cm^{2} [27]) quadrupole-induced broadening[4c,f,28] and/or surface inhomogeneities. Therefore, this signal is assigned to a surface Al−$^{13}CH_3$ functionality (a labeled methide group transferred to a DA surface Lewis acid center) by comparison to established group 4 and actinide surface chemistry (e.g., δ −12.8 in $Cp_2Zr(^{13}CH_3)_2$/DA,[4b] δ −13 in $Cp'_2Th(^{13}CH_3)_2$/DA[4c,d]). This observation suggests the formation of a "cation-like" Ta adsorbate (e.g., structure **F**) on DA, and the downfield-shifted Ta−$^{13}CH_3$ signal at δ 72 strongly supports this assignment. The signature of a μ-oxo adsorbate (structure **G**) is also detected at δ 60, based on the results above for **1***/PDS. The breadth of the Ta−CH_3 signals may reflect, among other factors, $^{13}C-^{181}Ta$ (^{181}Ta: $I = {}^{7}/_{2}$, $Q = 3e \times 10^{-24}$ cm^{2} [27]) quadrupolar interactions[28] or scalar coupling.[29]

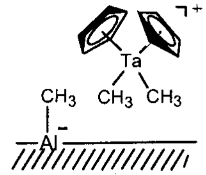


F

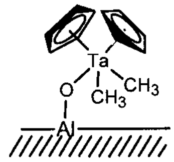


G

Figure 2 shows the solid-state ^{13}C CPMAS NMR spectrum of complex **2***, $Cp_2Ta(^{13}CH_3)_3$, adsorbed on three different high surface area oxide supports. In Figure 2A, the CPMAS spectrum of **2***/DA contains patterns similar to those of **1***/DA (Figure 1B). Thus, two labeled Ta−$^{13}CH_3$ resonances are observed at δ 53 and 19. The signal at δ 53 is assigned to a "cation-like" Ta−$^{13}CH_3$ species (structure **H**) by analogy to δ(Ta−CH_3) data for $Cp_2Ta(CH_3)_2^+(C_6F_5)_3AlCH_3Al(C_6F_5)_3^-$ (δ 57.05)[30]and $Cp_2Ta(CH_3)_2^+B(C_6F_5)_4^-$ (δ 55.6).[31] As previously discussed, the broad resonance at δ −14 can be assigned to the Al−$^{13}\boldsymbol{C}H_3$ moiety and the one at δ 114 to a $\boldsymbol{C}_5H_5$ signal. As for a signal at δ 19, the upfield displacement of δ(Ta−$^{13}\mathbf{C}H_3$) from that in neat complex **2** at δ 21.6 suggests, by analogy to supported organoactinide and group 4 results,[4c−f] formation of a $Cp_2Ta(^{13}\mathbf{C}H_3)_2O-$ μ-oxo species (structure **I**).[32,33]

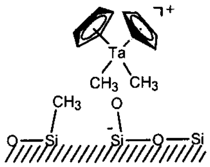


H



I

Figure 2B presents the CPMAS spectrum of complex **2*** (∼0.18 Ta nm^{-2}) chemisorbed on highly dehydroxylated silica (∼0.4 σ-OH nm^{-2}).[22] Signals assignable to Cp ring carbon atoms (δ 114) and a μ-oxo $Cp_2Ta(^{13}\mathbf{C}H_3)_2O-$ species (δ 15) are clearly identifiable. The two major ^{13}C methyl signals at far upfield (δ −9) and downfield (δ 58) positions are also noteworthy. The resonance at δ −9 can be assigned to a surface Si−$^{13}\mathbf{C}H_3$ group. This signal at δ −9 indicates that the bulk of complex **2*** undergoes chemisorption on DS to form a species such as structure **J**, possibly via surface Si−O cleavage in a way analogous to metallocene dialkyl + DS[6] as discussed above.



J

Surprisingly, the signal at δ 58 is clearly a "cation-like" species as for **2***/DA, and this observation suggests that the resulting,

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(27) Brevard, C.; Granger, P. *Handbook of High-Resolution Multinuclear NMR*; John Wiley & Sons: New York, 1981.

(28) For discussions of residual solid-state dipolar interactions between quadrupolar and spin-$^{1}/_{2}$ nuclei, see: (a) Wi, S.; Frydman, V.; Frydman, L. *J. Chem. Phys.* **2001**, *114*, 8511−8519. (b) Hayashi, S. *Magn. Reson. Chem.* **1999**, *37*, 843−851. (c) Eichele, K.; Lumsden, M. D.; Wasylishen, R. E. *J. Phys. Chem.* **1993**, *97*, 8909−8916. (d) Olivieri, A. C. *J. Magn. Reson.* **1989**, *81*, 201−205. (e) Harris, R. K.; Nesbitt, G. J. *J. Magn. Reson.* **1988**, *77*, 348−355. (f) Olivieri, A. C.; Frydman, L.; Grasselli, M.; Diaz, L. E. *J. Magn. Reson.* **1988**, *76*, 281−289.

(29) Several examples of heteronuclear metal-(C, B, or P) scalar couplings in CPMAS experiments have been reported, see: (a) Bowmaker, G. A.; Effendy; Hanna, J. V.; Healy, P. C.; Reid, J. C.; Rickard, C. E. F.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2000**, *5*, 753−762. (b) Wrackmeyer, B.; Klaus, U.; Milius, W.; Klaus, E.; Schaller, T. *J. Organomet. Chem.* **1996**, *517*, 235−242. (c) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Pohmer, K. *Inorg. Chem.* **1991**, *30*, 1102−1107. (d) Kendrick, R. D.; Yannoni, C. S.; Aikman, R.; Lagow, R. J. *J. Magn. Reson.* **1980**, *37*, 555−556.

(30) Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 5541−5543.

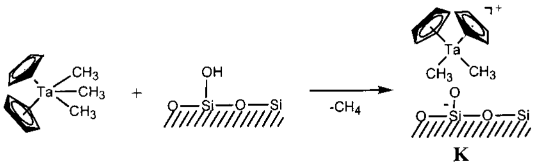
(31) Cook, K. S.; Piers, W. E.; Rettig, S. J.; McDonald, R. *Organometallics* **2000**, *19*, 2243−2245.

(32) (a) A weakly acidic silanol, Ph_3SiOH (pK_a = 10.8), does not undergo reaction with Cp_2TaMe_3 (**2**) at 20 °C in toluene over the course of several days, and the reaction mixture begins to decompose at elevated temperatures (70 °C). (b) In the close analogues $Cp_2(CH_3)Ta(\mu\text{-}O)Re[C(CH_3)=CH_2](CO)_4$ and $Cp_2(CH_3)Ta(\mu\text{-}\eta^1{:}\eta^2{:}\eta^3\text{-}C_3H_2O_2)Fe_2(CO)_7$, δ (Ta−CH_3) occurs at 15.8 and 36.38, respectively.[32c] (c) Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 1981−1996.

(33) (a) Alternatively, two other assignments are conceivable. (i) A physisorbed complex. We exclude this possibility because the sample was subjected to thorough washing steps. (ii) A product arising from Cp ring protonolysis. The observed spectral parameter is not in agreement with that of a reported model complex, $Ta(CH_3)_3(OAr')_2$ [δ(Ta-$^{13}CH_3$) = 66.8, Ar′ = 2,6-di-^{t}butylphenyl].[33b] (b) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502−1509.

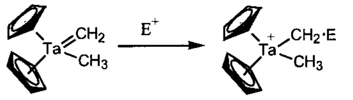
methylated DS surface serves as a "weakly coordinating anion"− to date an unprecedented cation-forming reaction mode. This observation stands in sharp contrast to the reported DS surface chemistry of organo-group 4 and actinide complexes, the hydrocarbyl complexes of which exclusively form μ-oxo species (structure **C**) as well as Si−CH$_3$ groups.[6] The present assignments are further supported by ^{13}C CPMAS experiments on nonlabeled Cp$_2$Ta(CH$_3$)$_3$(**2**)/DS, where the resonances assigned to ^{13}C labeled methyl carbons at δ 58, 15, and −9 are not detected, and only the weak Cp ring carbon signal is detected at δ 112.

The solid-state ^{13}C CPMAS spectrum of **2***/PDS strongly supports this striking Cp$_2$Ta(CH$_3$)$_3$ reactivity model (Figure 2C). A Si−^{13}CH$_3$ resonance is not observable as expected, but rather an intense "cation-like" Ta−^{13}CH$_3$ resonance is detected at δ 58, which is in accord with the above results, that is, the formation of structure **K** (eq 7). In support of this assignment, in situ ^{1}H NMR-scale slurry experiments reveal the evolution of methane (δ 0.15 in C$_6$D$_6$). Again, the occurrence of a relatively weak resonance at δ 18 is analogously assigned to small quantities of a Cp$_2$Ta(^{13}**C**H$_3$)$_2$O− species.

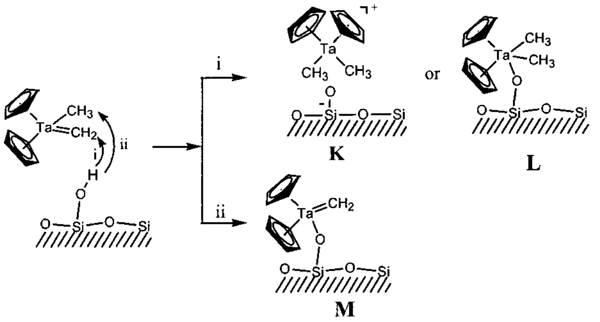


(7)

Chemisorption of alkylidene complex **3***, Cp$_2$Ta(^{13}CH$_2$)(^{13}CH$_3$), on PDS was conducted to explore the fate of a group 5 complex having an alkylidene functionality (Figure 3A). On the basis of known solution phase reaction patterns and theoretical results,[34] electrophiles such as a proton in the case of PDS might be expected to (i) attack the alkylidene α-carbon atom to yield a methyl group (structure **K** and/or **L**) which has considerable precedent (eq 8)[16,31] or (ii) protonolyze a Ta−methyl bond to form a μ-oxo alkylidene complex (structure **M**)[35] as depicted in pathway (ii), eq 9. Interestingly, Figure 3A reveals two **3***/PDS Ta−^{13}**C**H$_3$ resonances at δ 57 (major) and 18 (minor) and that there is no evidence for formation of a μ-oxo alkylidene type complex (e.g., structure **M**). It cannot be totally excluded that ^{13}C−^{181}Ta quadrupolar-induced interactions[28] and/or scalar coupling[29,36] to some degree broaden or split the solid-state alkylidene C$_\alpha$ signal. However, on the basis of the observations that in the ^{13}C CPMAS solid-state NMR spectrum of neat **3***, the alkylidene carbon resonance can be clearly assigned at δ 225.7 (Table 1) and that an alkylidene signal at δ 247 is readily detected in **4***/PDS (vide infra), the alkylidene carbon resonance of **3***/PDS, if present, should be detectable using the present spectral acquisition parameters. The spectrum of **3***/PDS is virtually identical to that of **2***/PDS (Figure 2C), and the CPMAS data therefore argue that complex **3*** undergoes chemisorption on PDA via pathway (i) (eq 9), but to predominantly form cationic structure **K** [δ(Ta−^{13}CH$_3$) = 57] without major involvement of the silica surface Si−O$^-$ moieties which would yield structure **L** (δ(Ta−^{13}CH$_3$) = 18). These assignments are again supported by ^{13}C CPMAS data on unlabeled Cp$_2$Ta(CH$_2$)(CH$_3$)(**3**)/PDS, where the resonances assigned to ^{13}C labeled methyl carbons at δ 57 and 18 are not detected, while the weak Cp ring carbon signal is again observed at δ 113.



(8)



(9)

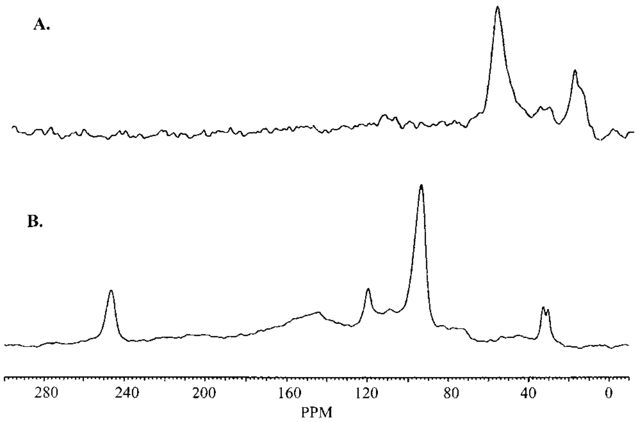


Figure 3. (A) ^{13}C CPMAS NMR spectrum of Cp$_2$Ta(^{13}CH$_2$)(^{13}CH$_3$) (**3***)/PDS (12 000 scans, repetition time = 4 s, contact time = 2.6 ms, spinning speed = 6.7 kHz). (B) ^{13}C Bloch-decay NMR spectrum of Ta(^{13}CH$_2{}^t$Bu)$_3$(^{13}CH^{t}Bu) (**4***)/PDS (90° pulse sequence: 4750 scans, repetition time = 4 s, spinning speed = 6.2 kHz).

The chemisorptive pathways of non-Cp Ta alkylidene complex **4***, Ta(^{13}CH^{t}Bu)(^{13}CH$_2{}^t$Bu)$_3$, were investigated on PDS and compared to those forming **3***/PDS (Figure 3). From Figure 3B, the most disparate feature of the surface chemistry of alkylidene complexes **3*** and **4*** on PDS is that complex **4*** retains the alkylidene functionality (an intense resonance at δ 247) rather than forming a "cation-like" species. Accompanying this resonance are a weak neopentyl C$_\alpha$ feature at δ 120.7 and a major neopentyl C$_\alpha$ resonance at δ 95.1. These assignments are confirmed by the observation that none of these resonances are detected in the ^{13}C CPMAS NMR spectrum of unlabeled **4**/PDS. Two resonances at δ 33.9 and 32.0, also observable in the spectrum of unlabeled adsorbate **4**/PDS, are assignable to the neopentyl C$_\gamma$ and neopentylidene C$_\gamma$ signals, respectively. To identify structural/spectral correlations with structures of known complexes, analogous siloxy/alkoxy−tantalum compounds and their ^{13}C NMR parameters (structures **N**, **O**, **P**)[26b] are compared with data for the proposed structure of **4***/PDS (structures **Q**, **R**, **S**) in Figure 4. The ^{13}C NMR parameters of

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(34) Cook, K. S.; Piers, W. E.; Rettig, S. J. *Organometallics* **1999**, *18*, 1575−1577.

(35) This type of reaction has been reported for organo-Re and organo-Mo complexes, see: (a) ref 15. (b) ref 11a.

(36) In the ^{13}C solution NMR spectrum of α-^{13}C enriched complex **3***, sharp singlets are observed for all ^{13}C$_\alpha$ signals (including alkylidene C$_\alpha$), suggesting that the magnitude of Ta-^{13}C$_\alpha$ scalar coupling is not great or that the ^{181}Ta T_1 is very short.

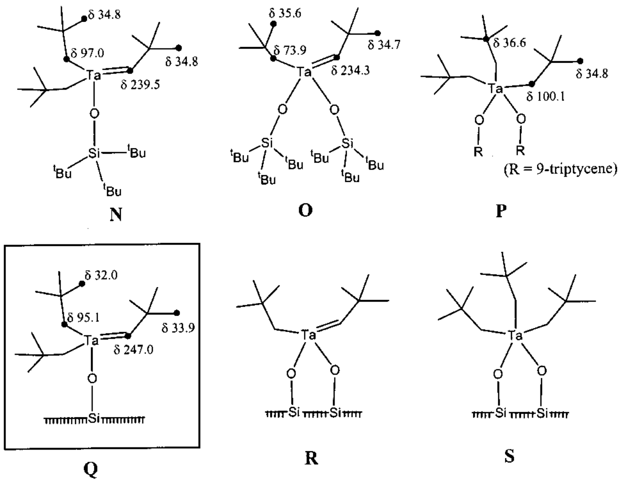
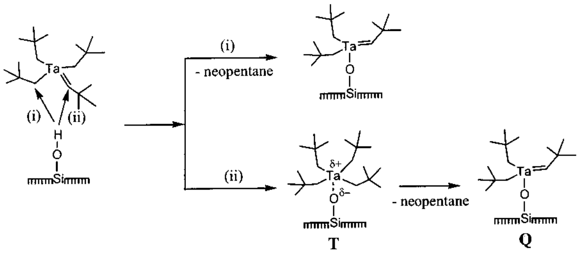


Figure 4. Reported siloxy- and alkoxy-organotantalum complexes (structures **N**, **O**, and **P**), proposed structure of surface adsorbate **4***/PDS (structure **Q**) together with ^{13}C NMR parameters, and other analogous structures (**R** and **S**).

structure **L** (δ 239.5, 97.0, 34.8, and 34.8) can be the most closely correlated with those of **4***/PDS (δ 247, 95.1, 33.9, and 32.0), and therefore, structure **Q**, analogous to structure **N**, is proposed to be the major chemisorptive product on PDS. To yield adsorbate **Q**, proton transfer could, in principle, proceed via either of the pathways suggested in eq 10 (in an in situ slurry ^{1}H NMR-scale experiment, neopentane evolution is detected at δ 0.94 in C_6D_{12}). With the present ^{13}C NMR results,



(10)

it is proposed that a proton transfers to (i) a neopentyl group, or (ii) a neopentylidene group to yield "unstable" tetraneopentyl Ta species, **T**, which subsequently undergoes α-elimination to yield structure **Q** and neopentane (eq 10).[37] Although a weak resonance at δ 120.7 cannot be rigorously assigned, it may arise from surface species such as cationic structure **T** (eq 10), which are "stabilized" on certain PDS sites. The assignment of structure **T** is supported by the following observations: (a) the ^{13}C solid-state NMR spectrum of unlabeled complex **4**/PDS exhibits only signals in the methyl region which suggests that the resonance at δ 120.7 is from a ^{13}C-enriched *methylene* carbon (i.e., C_α), (b) the resonance is low-field shifted from those of complex **4** (neopentyl C_α, δ 114.1) or species **Q** (neopentyl C_α, δ 95.1), suggesting an "electron-deficient" metal environment, and (c) the formation of cationic **T** is analogous to the fate of **3*** on PDS. Therefore, the present study argues that a well-defined species of structure **Q** is formed as the dominant species on PDS, while a structure such as **T** is a minor species.

These results stand in sharp contrast to previous chemisorption studies with **4** which proposed the formation of a ~50:50[37b] or a 65:35 mixture[37c] of structures **Q** and **R** on PDS on the basis of evolved neopentane, alcoholysis experiments, IR spectroscopy, and elemental analyses. The present work shows that if a di-μ-oxo species (structure **R**) were present, it would exhibit a significant neopentyl C_α resonance at ~δ 75 and an additional low-field neopentylidene C_α resonance at $\gtrsim\delta$ 234, as evidenced by the spectral parameters exhibited by model compound **O** (Figure 4).[26b] Such features, however, are not observed in the present CPMAS ^{13}C NMR and Bloch decay spectra (Figure 3B).[38] Furthermore, note the broad signal at ~δ 150 in Figure 3B, which suggests that some portion of complex **4** undergoes unidentified reaction(s) or decomposition, which to some degree complicates structural arguments. An alternative pathway to a Ta bisalkoxide (i.e., structure **S** analogous to structure **P**) that has precedent in known solution phase chemistry (eq 11) can also be invoked.[26b] Nevertheless, the formation of adsorbate **S**

$$\underset{\mathbf{4}}{\mathrm{Np_3Ta{=}C(H)C(CH_3)_3}} + 2\mathrm{ROH} \xrightarrow[\text{benzene}]{25\ ^\circ\mathrm{C}} \underset{\text{(structure }\mathbf{P})}{\mathrm{Np_3Ta(OR)_2}} + \mathrm{NpH} \quad (11)$$

(≈**P**) cannot be a major surface chemistry pathway because it would exhibit a neopentyl C_α resonance at ~δ 100 and no neopentylidene C_α resonance, in contrast to what is detected here.

In summary, the present high-resolution solid-state ^{13}C NMR studies of organotantalum chemisorption pathways reveal two striking features. First, mono Cp (**1***) and bis Cp (**2***) tantalum hydrocarbyls react with surface Si−OH groups on PDS via disparate pathways to yield predominantly neutral μ-oxo-(structure **D**) for **1*** and "cationic" (structure **K**) species for **2***, respectively. This difference would appear to reflect a combination of electronic (14e for **1*** vs 18e for **2***) and steric factors; for example, the Ta center of **2***/PDS ($Cp_2TaMe_2^+$, Σ(cone angles) ≈ 420°)[20] is somewhat more crowded than that of **1***($Cp'TaMe_3^+$, Σ(cone angles) ≈ 412°).[20] In support of this cationic adsorbate formation on weak Brønsted acidic surfaces, note that while $Cp_2Zr(CH_3)(OTf)$ is known as a neutral, covalent μ-oxo complex,[39] analogous $CpCp'Ta(CH_3)_2^+OTf^-$ is ionic.[40] Second, chemisorption of the two Ta alkylidene complexes, **3*** and **4***, proceeds via very different pathways to yield "cation-like" (structure **K**) and μ-oxo-"alkylidene" species (structure **Q**), respectively. Such disparate reactivity patterns again must arise from combined electronic (formally 18e for **3*** and 10e for **4***) and steric factors.

Concluding Remarks

The present ^{13}C CPMAS NMR spectroscopic study of tantalum hydrocarbyl and alkylidene complex chemisorption on

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(37) (a) In analogous work which reported chemisorption via sublimation of **4** onto fumed silica calcined at 500 °C, analysis of evolved neopentane during the chemisorption of complex **4** on deuterated PDS detected d_0- and d_2-neopentane, and the chemisorption process was proposed to occur via pathway (ii) in eq 10.[37c] (b) Lefort, L.; Chabanas, M.; Maury, O.; Meunier, D.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M. *J. Organomet. Chem.* **2000**, *593−594*, 96−100. (c) Dufaud, V.; Niccolai, G. P.; Thivolle-Cazat, J.; Basset, J.-M. *J. Am. Chem. Soc.* **1995**, *117*, 4288−4294.

(38) A Bloch decay pulse sequence is employed to obtain a spectrum somewhat less sensitive to carbon type, that is, alkyl C_α versus alkylidene C_α (Figure 3B). However, the ^{13}C CPMAS spectrum of **4***/PDS exhibits the same features as the Figure 3B except different relative intensities, that is, a higher intensity ratio of alkyl C_α versus alkylidene C_α. The intensity of the weak signal at δ 71 is slightly enhanced, but is still very marginal as compared to that of the signal at δ 95.1.

(39) Toscano, P. J.; Marks, T. J., unpublished results.

(40) Schaefer, W. P.; Quan, R. W.; Bercaw, J. E. *Acta Crystallogr.* **1992**, *C48*, 1610−1612.

high surface area metal oxides illustrates the great utility of this technique for characterizing organometallic molecule−surface interactions. Silica is thought to be a virtually inert support due to its low acidity and basicity.[41] However, to our knowledge, this work represents the first case in which a "cationic-like" organometallic species has been detected on the surface of unmodified silica. Additionally, for the first time, solid-state ^{13}C NMR studies successfully delineate and differentiate two characteristic surface reaction modes for tantalum alkylidene complex chemisorption. Further studies of the reactivities of the present surface adsorbates and supported alkylidene complexes are in progress.

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(41) Tanabe, K. *Solid Acids and Bases-Their Catalytic Properties*; Academic Press: Tokyo, New York, London, 1970; Chapter 4, pp 53−54.