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Ammonia and Dinitrogen Activation by Surface Organometallic Chemistry on Silica-Grafted Tantalum Hydrides

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Ammonia N–H bond activation and dinitrogen N≡N cleavage with dihydrogen on an isolated metal atom have been achieved with the silica-grafted Ta^{III} and Ta^{V} hydrides [(≡SiO)$_2$TaH] (**2a**) and [(≡SiO)$_2$TaH$_3$] (**2b**), accessed through surface organometallic chemistry (SOMC). The synthesis of the starting tantalum hydrides **2a** and **2b** by grafting tris(neopentyl)neopentylidenetantalum(V), Ta(=CH–*t*Bu)Np$_3$, on silica yields well-defined, isolated tantalum atoms. Silsesquioxane molecular modelling shows that the mechanism of the grafting reaction implies a tetraalkyl intermediate [(≡SiO)TaNp$_4$]. The starting hydrides **2a** and **2b** react stoichiometrically and catalytically with alkanes in reactions such as alkane metathesis, cross-metathesis between ethane and toluene, and methane coupling to form ethane. Mechanistic studies show the relevance of tantalum carbenes and Chauvin-like metallacyclobutane intermediates in most of these reactions. Finally, the stoichiometric N_2 cleavage and NH_3 activation to the final imido amido tantalum(V) complex [(≡SiO)$_2$Ta(NH)(NH$_2$)] (**3**) are reviewed and discussed mechanistically. In the N≡N cleavage reaction, dihydrogen adducts on silica-grafted isolated tantalum atoms appear to play a central role. The ammonia reaction occurs by bifunctional activation through the Lewis acid/Lewis base couple formed by a metal centre and a coordinated nitrogen atom, the so-called "NH effect". Such bifunctional activation is also observed for the heterolytic cleavage of H_2 by [(≡SiO)$_2$Ta(NH)(NH$_2$)] (**3**).

1. Introduction

The development of single-site heterogeneous catalysts has been the main aim of the surface organometallic chemistry (SOMC) approach,[1] which is based on the application of molecular organometallic chemistry principles to the development of well-defined surface-grafted metallic complexes on oxide supports. Studies in heterogeneous catalysis spanning over several decades have contributed to the assessment of SOMC as a viable route to high-performance catalysts. As examples of its success, one could mention systems such as silica-grafted olefin metathesis catalysts with a TON of 231000 in 1500 min for propene,[2] the trifunctional tungsten-based catalyst for direct conversion of ethylene to propylene[3] and the tantalum-based catalytic system for the non-oxidative coupling of methane to form ethane.[4] This final tantalum-based system, which contains at least the two surface tantalum hydride species, [(≡SiO)$_2$TaH] and [(≡SiO)$_2$TaH$_3$],[5] has displayed remarkable activity toward C–C and C–H bonds in both stoichiometric activation[6] and catalytic reactions such as alkane metathesis,[7] cross-metathesis between ethane and toluene,[8] and methane coupling to form ethane.[4]

More recently, the same starting hydrides [(≡SiO)$_2$TaH] and [(≡SiO)$_2$TaH$_3$] have been shown to activate the N–H bond of ammonia[9] and cleave the dinitrogen triple bond.[10] This paper will review these recent advances around silica-supported tantalum hydrides in the context of this unique N≡N triple bond cleavage with H_2 on an isolated metal atom and try to offer an explanation for the lack of similar precedents in molecular, heterogeneous or enzymatic systems. In particular, it will show that the ability of SOMC to anchor isolated metal atoms on a surface distinguishes it both from heterogeneous and molecular systems by creating single-centre catalyst sites that are able to overcome some of the limitations of either heterogeneous or homogeneous catalysts.

2. Synthesis and Characterization of Starting Silica-Supported Tantalum Hydrides

2.1. Synthesis and Characterization of Silica-Supported Tantalum Alkyl Precursors [(≡SiO)Ta(=CH-*t*Bu)Np$_2$] (1a) and [(≡SiO)$_2$Ta(=CH-*t*Bu)Np] (1b)

The isolation of well-defined single metal atoms grafted on silica relies on mastery of the initial chemisorption step, which entails both the use of the appropriate organometallic precursor and control over the preparation of the support.[1] In the case of silica-grafted tantalum precursors,

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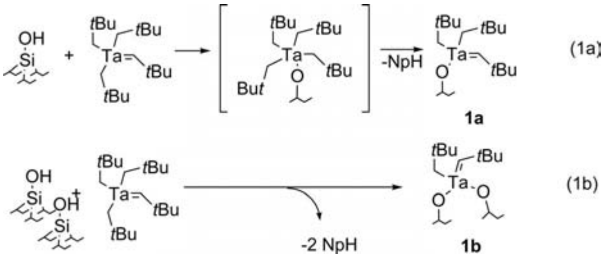
grafting of the tantalum organometallic precursor tris(neopentyl)neopentylidenetantalum(V), Ta(=CH-*t*Bu)Np$_3$ (Np = CH$_2$CMe$_3$),[11] onto silica is achieved through surface organometallic procedures analogous to those employed for other metals (e.g., Hf, Zr, Ti).[12–15] Sublimation or impregnation of the volatile perhydrocarbyl precursor Ta(=CH-*t*Bu)Np$_3$ onto a partially dehydroxylated silica surface leads to the formation of the grafted organometallic species [(≡SiO)Ta(=CH-*t*Bu)Np$_2$] (**1a**) and [(≡SiO)$_2$Ta(=CH-*t*Bu)-Np] (**1b**)[16] [see Equations (1a,b)], whose relative distribution can be controlled by the concentration of surface silanol groups generated during the dehydroxylation step.[17] The gaseous byproducts (viz. neopentane, CMe$_4$) are easily removable from the solid and can thus be quantified, leading to well-defined grafting stoichiometry.[18]



(1)

As is generally the case for this approach, silica dehydroxylated at 300 °C, $\mathrm{SiO}_{2-(300)}$, yields primarily the bipodal tantalum(V) species **1b**, silica dehydroxylated at 700 °C, $\mathrm{SiO}_{2-(700)}$, yields only the monopodal tantalum(V) species **1a**, while silica dehydroxylated at 500 °C, $\mathrm{SiO}_{2-(500)}$, yields a mixture of the mono- and bipodal species.[18] On MCM-41 mesoporous silica dehydroxylated at 500 °C, MCM-41$_{-(500)}$, however, the monopodal species is formed almost exclusively.[5] This mesostructured siliceous support also has the advantage of increased tantalum loading (typically 15% by weight vs. 5% for flame silica).[5]

Extensive characterization and mechanistic investigations by several in situ techniques have allowed a precise molecular description of the silica-grafted complexes [(≡SiO)Ta(=CH-*t*Bu)Np$_2$] and [(≡SiO)$_2$Ta(=CH-*t*Bu)Np]. In IR spectroscopy, one observes a consumption of the ν(SiO–H) peak at 3747 cm^{-1} with a concomitant increase in the intensity of the ν(C–H) and δ(C–H) bands around 2900 and 1400 cm^{-1}, respectively.[16] Analysis of the gas phase reveals that, on average, one molecule of neopentane is evolved for each tantalum centre grafted onto $\mathrm{SiO}_{2-(700)}$[18] or MCM-41$_{-(500)}$.[5] For $\mathrm{SiO}_{2-(300)}$, this number is closer to 2, which is consistent with the formation of the digrafted species.[18] The ^{13}C CP/MAS SS NMR spectrum of the complex displays two broad peaks at 33 and 45 ppm, assigned to the methyl groups of the hydrocarbyl ligands and the quaternary carbon of the neopentylidene ligand, respectively.[16] The increased loading possible on MCM-41$_{-(500)}$ has also led to a better resolved ^{13}C MAS SS NMR spectrum, whose peaks can be assigned as follows: 33.4 ppm [*C*(CMe$_3$)$_3$], 45.7 ppm [C(*C*Me$_3$)$_3$], 95 ppm (*C*H$_2$-*t*Bu) and 247 ppm (=*C*H-*t*Bu).[5] The use of silsesquioxane molecular models[19–21] and advanced NMR spectroscopic techniques such as *J*-resolved 2D SS NMR, in particular, have helped describe the molecular structure of the grafted species down to the extent of the small $J_{\text{C–H}}$ coupling of the methylidene ligand (vide infra). Ta$^{\text{III}}$-edge spectroscopy EXAFS analysis for the monografted species is consistent with a first shell (at 1.898 Å) of metal neighbours consisting of one carbon atom and one oxygen atom, assigned to the carbenic C and the siloxy O atoms, a second shell (at 2.150 Å) of two carbon atoms, assigned to the methylene C of the neopentyl

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Alessandra Quadrelli earned her B.S. in chemistry in 1994 at Scuola Normale Superiore di Pisa and University of Pisa under F. Calderazzo's supervision, and her Ph.D. from the University of Maryland, studying open-shell organometallic hydrides with Rinaldo Poli. During her post-doc in the chemical laboratories of Cambridge University with B. F. G. Johnson, Alessandra worked on silsesquioxane models for well-defined heterogeneous catalysts, a field she continued in Pisa in 2001 and in Lyon with J.-M. Basset, as CNRS researcher. She is currently a confirmed CNRS researcher in the field of catalysis and organometallic chemistry and head of the sustainable development chair of the CPE Lyon school of engineering. Her current research interests are N_2 and NH_3 activation and, with C. Thieuleux, the development of novel functional materials such as metal–organic frameworks (MOFs), for the activation of SiH_4 and CO_2.

ligands, a third shell (at 2.64 Å) of a single oxygen atom (vide infra) and a fourth shell (at 3.417 Å) of three carbon atoms.[20] Elemental analysis, in particular the C/Ta ratio, has also been useful in characterizing the distribution of mono- and digrafted products.[5,16,18]

The grafted products [($\equiv$SiO)Ta(=CH-*t*Bu)Np$_2$] (**1a**) and [($\equiv$SiO)$_2$Ta(=CH-*t*Bu)Np] (**1b**) are highly electron-deficient (formally 10 e without the silica surface contributions), which is reflected by two structural features in the monografted product. First, EXAFS analysis indicates the presence of an additional oxygen atom at 2.64 Å which is assigned to the oxygen atom of a siloxy bridge; this O atom may be considered a 2 e donor to the tantalum centre.[20] Second, the $^1J_{CH}$ of the carbenic proton (80 Hz), determined by 2D *J*-resolved SS NMR spectroscopy, indicates that the Ta=C–H bond angle is highly distorted (85°), and strongly suggests the presence of an agostic interaction between the metal centre and the C–H bond.[20]

The grafting by SOMC of Ta(=CH$_2$-*t*Bu)Np$_3$ on silica can also be understood mechanistically. Deuterium labelling studies[16] and the synthesis of molecular analogues[19] have shed some light on the mechanism of this reaction [Equation (1a)], which occurs through silanol addition across the Ta=C double bond, giving the tetrakis(neopentyl)siloxy complex as the kinetic product.[19] This complex evolves neopentane through α-H abstraction to yield the monopodal grafted product **1a**. For a sufficiently high concentration of surface silanols, the process is presumably repeated across the newly formed Ta=C double bond to give the bipodal product **1b**.[16,18]

2.2. Synthesis and Characterization of Silica-Supported Tantalum Hydrides [($\equiv$SiO)$_2$TaH] (2a) and [($\equiv$SiO)$_2$TaH$_3$] (2b)

The well-defined surface tantalum(V) alkyl precursors [($\equiv$SiO)Ta(=CH-*t*Bu)Np$_2$] (**1a**) and [($\equiv$SiO)$_2$Ta(=CH-*t*Bu)Np] (**1b**) are a good starting point for the synthesis of well-defined monometallic hydrides. The metal isolation is due mainly to the mild-temperature grafting procedure of the peralkyl precursor outlined above. The formation of strong and inert Ta–O bonds is also a key to the conservation of the isolated metal site, since they are crucial in preventing metal mobility in the following high-temperature hydrogenolysis treatment outlined below (T = 150 °C). Such treatment usually leads to metal aggregates, a process also known as sintering, or ill-defined metallic species for precursors that are poorly isolated and/or weakly anchored inorganic or organometallic salts. When heated at 150 °C under an atmosphere of dry H$_2$, the grafted complexes **1a** and **1b** yield the supported tantalum hydrides **2**, of which the major product is the monohydride, that is, [($\equiv$SiO)$_2$TaH] (**2a**), along with [($\equiv$SiO)$_2$TaH$_3$] (**2b**) and the surface silicon hydrides [$\equiv$SiH] and [=SiH$_2$].[5,6] The product of surface embedment [($\equiv$SiO)$_3$Ta] is also present to a smaller extent. The coexistence of these species has been established spectroscopically by EXAFS, IR and solid-state MAS ^{1}H NMR spectroscopy (Figure 1).

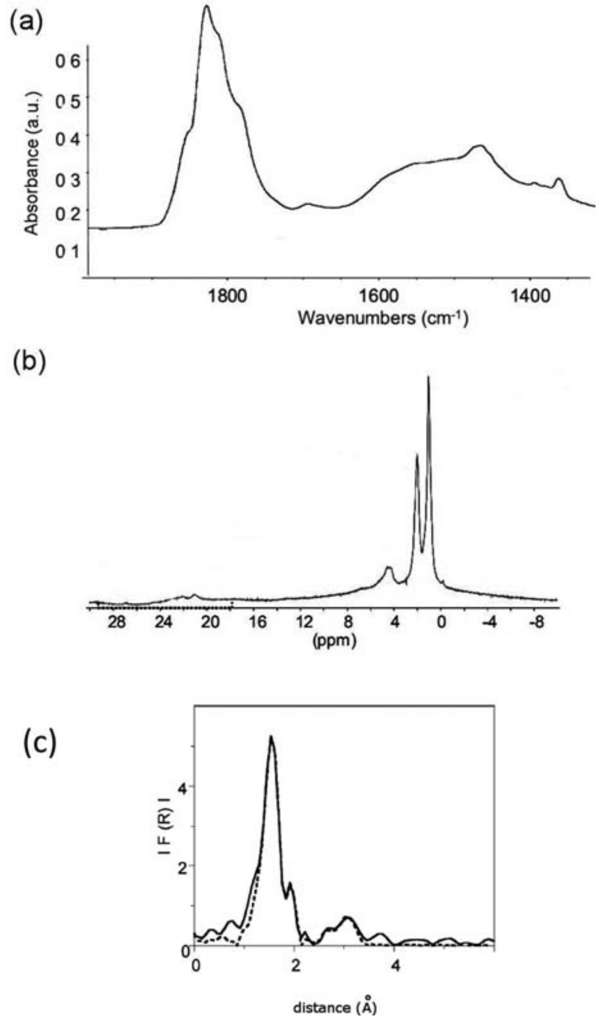
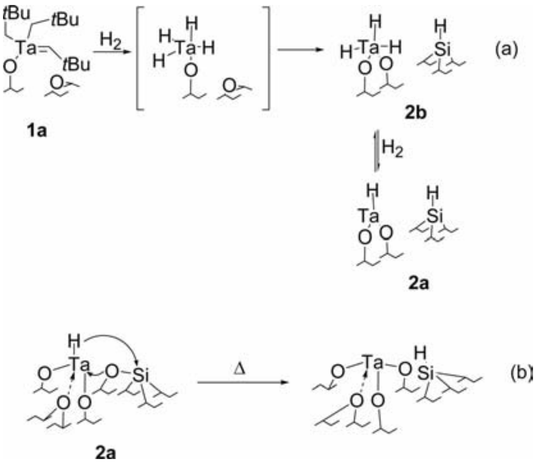


Figure 1. IR (a), ^{1}H MAS SS NMR (b) spectra and Fourier transform of Ta L$_{III}$-edge k3 EXAFS signal of the MCM-41-supported tantalum hydrides [($\equiv$SiO)$_2$TaH] (**2a**) and [($\equiv$SiO)$_2$TaH$_3$] (**2b**).

Ta L^{III}-edge EXAFS analysis is consistent with a bis(siloxy) surface species as the major surface species, with long-range interactions from bridging oxygen atoms of adjacent siloxy surface species [$\equiv$SiOSi$\equiv$], analogous to that observed for the grafted alkylidene described in the previous section.[6] The EXAFS study also shows well the complexity of the mixture: it suggests that the first coordination sphere of a tantalum centre consists, on average, of 2.3 oxygen atoms at 1.91 Å, 0.5 oxygen atoms at 2.91 Å and 0.4 oxygen atoms at 2.66 Å.[5] In addition, the EXAFS study shows that bimetallic Ta–Ta interactions, if any, are not significant,[5] thus supporting that the distance between the tantalum centres is maintained after the hydrogenolysis step. The IR spectrum of the products reveals new bands corresponding to ν(Ta–H) (1830 cm^{-1}) and ν(Si–H) (2215 cm^{-1}, 2270 cm^{-1}, 2300 cm^{-1}), as well as nearly complete consumption of the ν(C–H) and δ(C–H) bands.[6] Solid-state magic angle spinning ^{1}H NMR spectroscopy has also been used to characterize the tantalum hydrides on MCM-41$_{-(500)}$: weak signals between 20 and 30 ppm in the ^{1}H MAS SS NMR spectrum are indicative of the presence of tantalum hydrides, while the peak at 4.4 ppm is assigned to silicon hydrides.[5]

The mechanism for the formation of the surface tantalum hydride species **2** is proposed to proceed through a tetrahydride intermediate that cleaves a neighbouring siloxy bridge through hydride transfer to form a bipodal tantalum hydride and the surface silicon hydride [Equation (2a)].[5] The relative proportion of the tris(hydride) form can be estimated by heating the hydrides under vacuum at 150 °C. A 40 % decrease in the intensity of the ν(Ta–H) band was observed under these conditions.[5]



(2)

Through an analogous mechanism, when hydrides **2a** and **2b** are heated under dihydrogen at temperatures above 150 °C, the IR spectrum reveals an increase in the intensity of the ν(Si–H) band at 2240 cm^{-1} with a simultaneous decrease in that of the ν(Ta–H) band at 1830 cm^{-1}.[22] These observations are explained by hydride transfer to the silica surface through cleavage of a neighbouring siloxy bridge [Equation (2b)].[5,22] Thus, the hydride is transformed into a tris(siloxy) tantalum(III) species, and surface silanes are formed. Although this tripodal species remains electronically and coordinatively unsaturated, it no longer catalyzes alkane metathesis or hydrogenolysis.[22]

The supported tantalum hydrides [(≡SiO)$_2$TaH] (**2a**) and [(≡SiO)$_2$TaH$_3$] (**2b**) are even more electronically unsaturated than their alkylidene precursors [with a formal 8 e$^-$ count for the monohydride **2a** and a 10 e count for the tris(hydride) **2b**, with no possibility of an agostic interaction as in the case of the tantalum(V) neopentylidene complexes **1**]. They may nonetheless interact with surface oxygen atoms from adjacent siloxy bridges [≡SiOSi≡] to relieve the electronic deficiency, as experimentally suggested by EXAFS data reported above (Figure 2).[5]

As might be expected of such electrophilic species, **2a** and **2b** form 1:1 adducts with PMe$_3$. Upon coordination of this ligand, the tantalum hydride loses its ability to catalyze C–H activation, described in the next section, but is able to oligomerize ethylene.[23]

Analysis of the gaseous products after formation of the tantalum hydrides **2** on MCM-41$_{-(500)}$ reveals that methane is the only product.[5] This is consistent with the ability of the tantalum hydrides to perform catalytic hydrogenolysis of the expected gaseous product, neopentane (vide infra).[6]

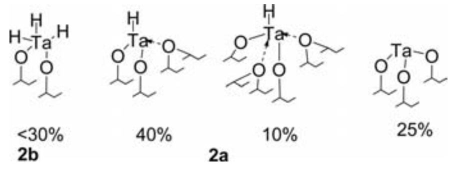
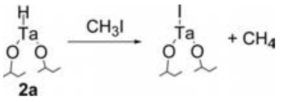
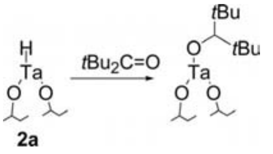


Figure 2. Distribution of silica-supported tantalum hydride species. Long-range interactions with siloxy bridges (≡Si–O–Si≡) may relieve electron deficiency at the metal centre.

The concentration of Ta–H bonds in the SiO$_{2-(500)}$ grafted complex was chemically determined by measuring by titration the quantity of released gases in reactions with methyl iodide, di-*tert*-butyl ketone and D$_2$O [Equations (3), (4) and (5)]. In each case, about one equivalent of hydride was found per tantalum atom.[6] The hydrides undergo reversible H/D exchange in the presence of the appropriate gas.[6]



(3)



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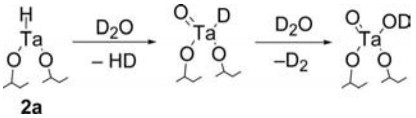
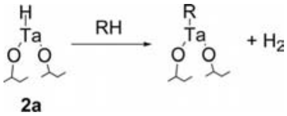


(5)

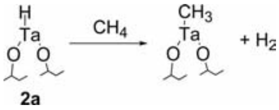
3. Reactivity of Silica-Supported Tantalum Hydrides with C–H and C–C Bonds

As might be expected of such highly electron-deficient species, the silica-supported tantalum hydrides [(≡SiO)$_2$TaH] (**2a**) and [(≡SiO)$_2$TaH$_3$] (**2b**) display high reactivity. For example, they are able to activate alkane C–C and C–H bonds.[24,25] The silica-supported tantalum hydrides stoichiometrically activate cycloalkane C–H bonds to form the Ta–cycloalkyl species with concomitant evolution of one equivalent of dihydrogen per C–H bond activated,[6] as shown in Equation (6) for the monohydride species.



(6)

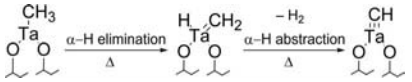
These tantalum surface alkyls readily react with molecular oxygen to give supported alkoxy oxo compounds and with water to liberate cycloalkane.[26] Hydride **2a** also reacts with methane to give a surface Ta–methyl species [Equation (7)].[26]



(7)

The tantalum hydrides can also catalyze H/D exchange between CD_4 and CH_4 and between CD_4 and H_2;[27] the initial rates are similar for both reactions, demonstrating that C–H bond activation is the rate-determining step in both cases.

When methane activation on the MCM-41-supported tantalum hydrides is followed by prolonged heating at 150 °C, the system evolves to tantalum methylidene hydride $[(\equiv SiO)_2TaH(=CH_2)]$ and the Ta–methylidyne complex $[(\equiv SiO)_2Ta(\equiv CH)]$, as evidenced by the appearance of new peaks in the ^{13}C CP/MAS SS NMR spectrum.[5] These species are presumably formed through α-H elimination or abstraction processes (Scheme 1), and the formation of the alkylidyne can be hindered under an increased pressure of H_2.[4] The methylidene hydride is proposed as a key intermediate in the catalytic cycle for alkane metathesis (vide infra).[28,29] Precedents exist for molecular organometallic alkylidyne complexes capable of activating C–H bonds.[30] The presence of such organometallic fragments even at higher temperatures reveals the relevance of SOMC in the broader context of heterogeneous catalysis. SOMC can explore high temperature ranges incompatible with traditional solution (homogeneous) organometallic chemistry, yet preserves the molecular characteristics and the chemical nature of crucial catalytic intermediates such as carbene and carbyne metal moieties on the active surface.

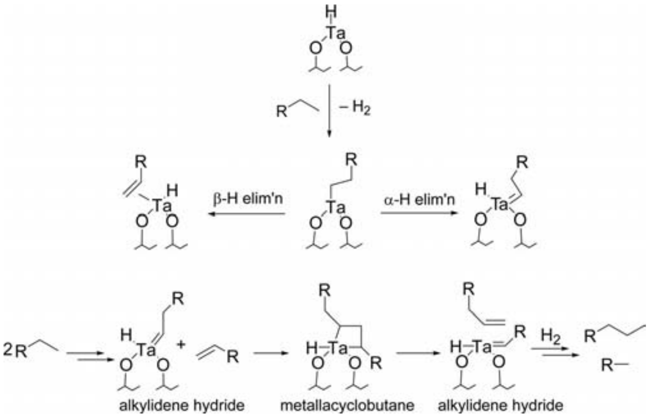


Scheme 1. Formation of tantalum alkylidene and alkylidyne species from the surface tantalum methyl species.

Tantalum hydrides **2** further react with acyclic alkanes to catalyze their hydrogenolysis, yielding methane as the sole product.[31] Unlike the supported group 4 hydrides $\{[(\equiv SiO)_2ZrH_2]$, $[(\equiv SiO)_3ZrH]$, $[(\equiv SiO)_2HfH_2]$ and $[(\equiv SiO)_3HfH]\}$,[14,15] whose hydrogenolysis activity on alkanes leads to a mixture of methane and ethane, the tantalum hydrides are also able to hydrogenolyze ethane, suggesting a distinct mode of reactivity for these complexes.[32] Mechanistically, this difference has been explained by invoking that group 4 hydrides catalyze the hydrogenolysis of the alkane skeleton through successive β-alkyl transfer steps, while tantalum hydrides act by a different mechanism, described below. Group 4 hydrides are therefore unable to cleave the final C–C bond of a longer chain. This hypothesis has been experimentally corroborated by the production of a 3:1 mixture of methane to ethane after neopentane hydrogenolysis.[32]

Important among the reactivity of tantalum hydrides $[(\equiv SiO)_2TaH]$ (**2a**) and $[(\equiv SiO)_2TaH_3]$ (**2b**) is their ability to catalyze alkane metathesis, which transforms a linear alkane into its higher and lower homologues;[7,12,13,33,34] relative to the known homogeneous systems, the tantalum hydrides perform this transformation with higher selectivity.[35]

Cross-metathesis between two alkanes[36] or between toluene and ethane[8] is also possible. The mechanism of alkane metathesis has been subject to intense investigation.[6,7,26–29,33] Mikhailov's DFT calculations supported a mechanism involving ethylene π complexes[37] without direct σ-bond metathesis.[38] Recent experimental data have revealed that the primary products of the reaction are olefins and dihydrogen; thus, a mechanism invoking tantalum carbenes and a metallocyclobutane intermediate, as observed in olefin metathesis, is proposed (Scheme 2),[28] which shows the bifunctional role of the tantalum hydrides acting as both dehydrogenation and olefin metathesis catalysts.



Scheme 2. Simplified alkane metathesis mechanism by single-metal systems $[(\equiv SiO)_2TaH]$ (**2a**) and $[(\equiv SiO)_2TaH_3]$ (**2b**).

While both recent reports[39,40] and initial work on alkane metathesis[41] (also referred to as "molecular redistribution reaction of alkanes") always involved a dual catalyst system (see Figure 3 for selected examples), the systems developed by SOMC for alkane metathesis[42–44] originate from a single system {either [Ta(=CH-*t*Bu)(CH_2-*t*Bu)$_3$] or W(≡C-*t*Bu)(CH_2-*t*Bu)$_3$]}, each grafted on the appropriate inorganic oxide. The alumina-supported tungsten system is particularly noteworthy, as it achieves high activities in alkane metathesis. Decreasing the number of ligands around the tantalum centre by grafting the hydride onto a silica-supported zirconium hydroxide also improved catalyst performance in alkane metathesis.[45]

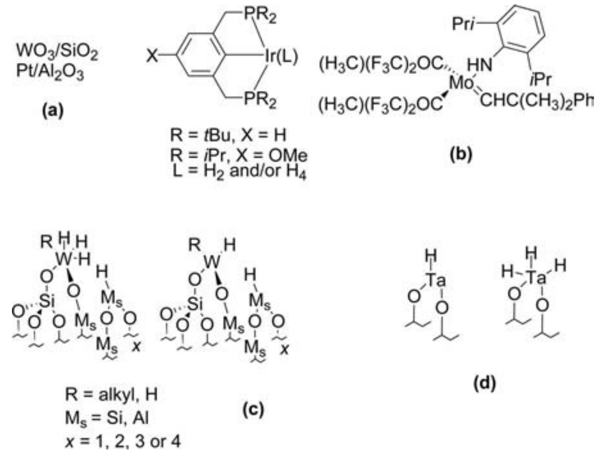
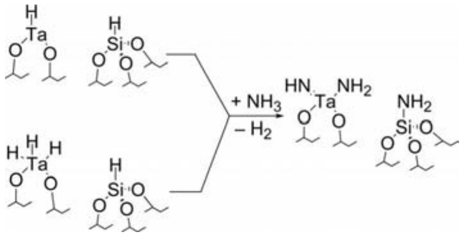


Figure 3. Selected examples of alkane metathesis catalysts: (a and b) dual catalyst systems vs. (c and d) single-metal systems developed by SOMC.

Rounding out this versatile reactivity with C–C and C–H bonds is the ability of **2** to perform non-oxidative coupling of methane.[4] Similarly to alkane metathesis, the key intermediate is a tantalum methylidene species, although the hydride is replaced with a methyl ligand in the case of non-oxidative coupling of methane. The proposed mechanism[4,34] postulates a migration of the methyl ligand onto the methylidene group of the species $[(\equiv SiO)_2TaMe(=CH_2)]$ followed by hydrogenoylsis of the resulting ethyl fragment to ethane. The proposed mechanism is based on a molecular organometallic precedent with $Cp^*{}_2Ta(=CH_2)CH_3$[46] and on the observed surface organometallic intermediates for the tantalum and tungsten systems. In any case, the relatively harsh experimental conditions required (250 °C, TON of about 10 after 100 h) indicate that this mechanism or any other is kinetically demanding.

4. Reactivity of Silica-Supported Tantalum Hydrides with N–H and N≡N Bonds

While alkane C–H bonds are well-established as a challenging site to activate,[25,47] ammonia N–H bonds are less readily identified as the challenge they can pose[48] and constitute an actively investigated field in organometallic chemistry.[49–59] Surface organometallic complexes **2**, $[(\equiv SiO)_2TaH]$ and $[(\equiv SiO)_2TaH_3]$, have achieved cleavage of the N–H bond of ammonia. The supported tantalum hydrides **2** react with NH_3 at room temperature to give the supported imido amido species $[(\equiv SiO)_2Ta(=NH)(NH_2)]$ (**3**) [Equation (8)].[9]



(8)

Surface silylamido species $[\equiv Si–NH_2]$ are also formed [Equation (8)] by room temperature reaction of NH_3 with surface silanes $[\equiv Si–H]$ present in the starting tantalum hydrides. This reaction occurs uniquely in the presence of tantalum; in the absence of the metal, surface silanes are unreactive towards NH_3, clearly showing the activating role of the metal centre in the reactivity of Si–H toward the otherwise inert ammonia.[9]

Product $[(\equiv SiO)_2Ta(=NH)(NH_2)]$ (**3**) has been thoroughly characterized by converging investigations based on elemental analysis, EXAFS analysis, IR and NMR spectroscopy. Characterization by SS MAS NMR spectroscopy of **3** has provided particular insight in understanding its structure. The use of heteronuclear ^{15}N-^{1}H and multiple-

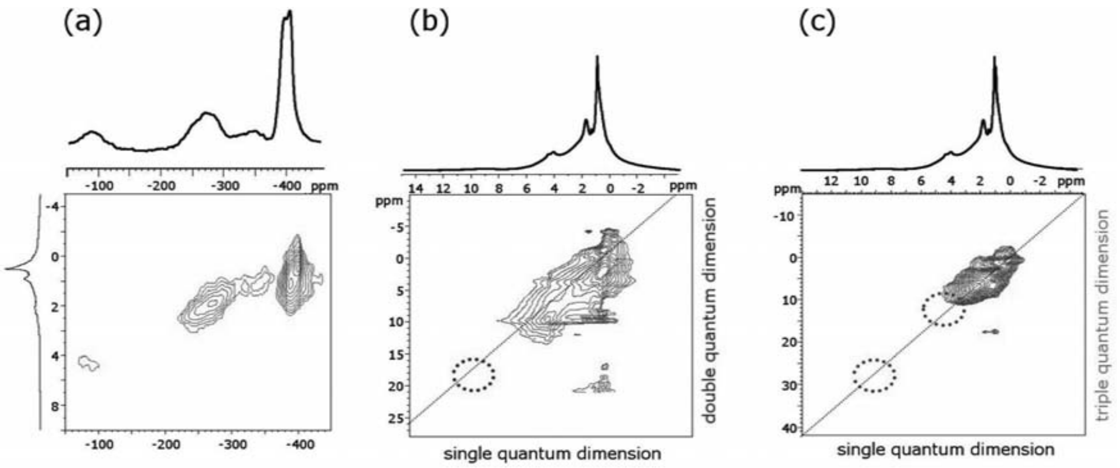


Figure 4. Two-dimensional solid-state MAS NMR spectra of the imido amido species $[(\equiv SiO)_2Ta(=NH)(NH_2)]$ (**3**) and its NH_3 adduct: (a) heteronuclear ^{15}N-^{1}H HETCOR, (b) ^{1}H double quantum (DQ), (c) ^{1}H triple quantum (TQ) spectra. Dotted ovals indicate the absence of autocorrelation peaks for the imido proton in DQ (b) and for the amido and imido protons in TQ (c) spectra.

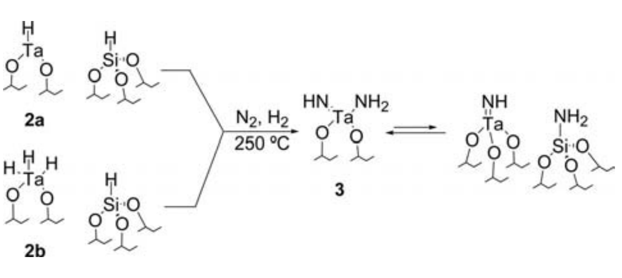
quantum ^1H-^1H experiments, namely double and triple quantum (DQ and TQ, respectively) on the fully ^{15}N labelled sample have permitted the assignment of the NMR signals (Figure 4). The TQ experiments, which were developed for the first time for this system,[9] have permitted the unambiguous detection and assignments of pairs and trios of equivalent protons in the imido amido species $[(\equiv SiO)_2Ta(=NH)(NH_2)]$ (**3**) as well as its ammonia adduct $[(\equiv SiO)_2Ta(=NH)(NH_2)(NH_3)]$ (**3·NH$_3$**). Through these methods, the ^1H resonances from the ammine (δ =2.2 ppm), amido (δ =4.3 ppm) and imido (δ =9.0 ppm) protons could be distinguished. Two-dimensional HETCOR experiments then allowed the assignment of the ^{15}N NMR signals: ammine (–340 ppm), amido (–270 ppm) and imido (–87 ppm) (Figure 4).[9]

Elemental analysis reveals that the solid contains 2.7 N/Ta, in good agreement with the formulated imido amido $[(\equiv SiO)_2Ta(=NH)(NH_2)]$ and surface silylamido products $[\equiv SiNH_2]$. Ta$^{\text{III}}$-edge EXAFS data support the proposed Ta$^{\text{V}}$ bis(siloxy) amido imido $[(\equiv SiO)_2Ta(=NH)(NH_2)]$ coordination sphere around the tantalum centre.[9] The IR spectrum of the product displays new bands corresponding to ν(N–H) and δ(N–H) at 3510–3330 cm^{-1} and 1605–1520 cm^{-1}, respectively. These assignments were confirmed through observation of the expected isotopic shifts by reaction of the imido amido species with D_2 to achieve H/D exchange or by reaction of the starting hydrides with $^{15}NH_3$ (Table 1).[9]

Table 1. IR stretching frequencies and their observed isotopic (^2H, ^{15}N) shifts. Calculated values are based on the reduced-mass spring approximation.

Starting frequencies [cm^{-1}]	Observed ^2H shift [cm^{-1}] (expected shift)	Observed ^{15}N shift [cm^{-1}] (expected shift)	Proposed assignment
3500	2597 (2556)	3490 (3492)	ν(N–H)
3462	2578 (2528)	3454 (3454)	ν(N–H)
3377	2474 (2468)	3372 (3369)	ν(N–H)
3293	2422 (2405)	3289 (3286)	ν(N–H) (NH_3)
1606	not obs. (1173)	1602 (1602)	δ(HNH) (NH_3)
1550	not obs. (1132)	1546 (1547)	δ(HNH) (Si–NH_2)
1521	not obs. (1110)	1516 (1518)	δ(HNH) (Ta–NH_2)

Even more surprisingly, tantalum hydrides **2a** and **2b** are able to cleave the strong and inert N≡N triple bond (bond energy: 225 kcal mol^{-1}; HOMO–LUMO gap: 22.9 eV).[60] The tantalum imido amido complex $[(\equiv SiO)_2Ta(=NH)(NH_2)]$ (**3**), reported above from the reaction of **2** with ammonia, can also be synthesized through reaction of a 1:1 mixture of dinitrogen and dihydrogen with surface hydrides **2** at 250 °C [Equation (9)].[10]



(9)

As in the case of ammonia, the products of the reaction have been characterized by IR spectroscopy, 2D HETCOR and DQ NMR spectroscopy, EXAFS and elemental analysis. Furthermore, DFT calculations on a model compound supported on a cristobalite (100) surface (Figure 5) have yielded optimized geometries, calculated IR stretching frequencies and NMR resonances comparable with experimental data.[10] DFT periodic calculations also provided thermodynamic insight into the nitrogen cleavage reaction by $[(\equiv SiO)_2TaH]$ and $[(\equiv SiO)_2TaH_3]$, showing a very exothermic reaction (–125.4 kcal mol^{-1} for dinitrogen cleavage), driven by the strength of the Ta(–NH_2) and Ta(=NH) bonds (Scheme 3).[10]

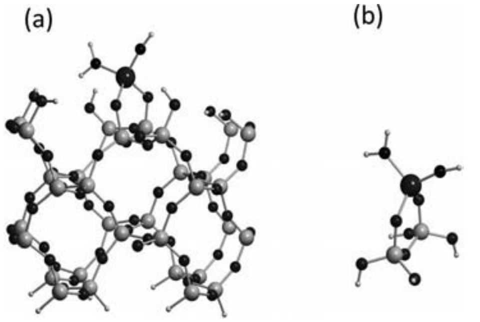
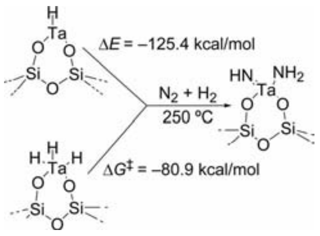
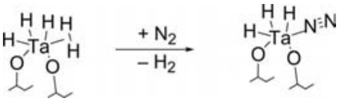


Figure 5. (a) DFT plane wave optimized structure of model $[(\equiv SiO)_2Ta(NH)(NH_2)]$, created by using β-cristobalite (100) as a surface model. (b) Model cluster compound $[(\mu\text{-}O)\{(HO)_2\text{-}SiO\}_2Ta^{V}(NH)(NH_2)]$.



Scheme 3. Calculated thermodynamic stability of model imido amido species relative to the model starting hydrides.

Preliminary mechanistic studies on the formation of the imido amido species by sequential addition of N_2 followed by H_2 support an initial reversible end-on coordination of N_2 to the tantalum centre at room temperature, as evidenced by a new band in the IR spectrum at 2280 cm^{-1}. Such coordination is more likely to occur at the electron-poor Ta$^{\text{V}}$ d^0 species $[(\equiv SiO)_2TaH_3]$ (**2b**), given the weak redshift with respect to free dinitrogen and the weak back-donation from the metal centre. The Ta$^{\text{III}}$ d^2 centre $[(\equiv SiO)_2TaH]$ (**2a**) would be expected to display increased back-bonding to coordinated N_2. Such coordination could also occur on some tantalum sites by displacement of coordinated dihydrogen, since 0.3 equiv. of H_2 are detected in the gas phase upon introduction of N_2.[10] Such evidence suggests the possible implication of a Ta$^{\text{V}}$ dihydrogen adduct among the surface species [Equation (10)].



(10)

Heating to 250 °C leads to a decrease in the intensity of this N_2 coordination band and the appearance of new bands consistent with ν(N–H) around 3400 cm^{-1}, indicative of an intermediate containing $Ta(N_2H_x)$ with reduced N–N bond order (diazenido or hydrazido). At this point, addition of H_2 leads to the formation of the final product.[10] As is already known for homogeneous and heterogeneous systems, the obstacle facing dinitrogen reduction to NH_x is not thermodynamic but kinetic.[60–62] The data observed for dinitrogen activation by the surface organometallic system $[(\equiv SiO)_2TaH]$ and $[(\equiv SiO)_2TaH_3]$ point to the same issues: while the transformation is exothermic, a large kinetic barrier remains in place.

5. Reactivity and Mechanism of Formation of Silica-Supported Tantalum(V) Imido Amido Complex $[(SiO)_2Ta(=NH)(NH_2)]$ (3)

The first studies on the reactivity of the imido amido complex $[(\equiv SiO)_2Ta(NH)(NH_2)]$ (**3**) have focused on its capability for H/D exchange. Gentle heating (60 °C, 3 h) under a deuterium atmosphere causes exchange of the protons on the imido and amido ligands for deuterium. This behaviour has been observed through the appropriate isotopic shifts in the IR spectra of the complexes and is reversible, since exposing the deuterated species to a hydrogen atmosphere regenerates the original imido amido species.[63]

The mechanism of this exchange reaction has been explored by DFT calculations on the model cluster compound $[\{(\mu\text{-}O)(HO)_2SiO\}_2Ta^V(NH)(NH_2)]$ (Figure 5b), with the Gaussian 03 package.[63] Heterolytic splitting of H_2 is the most favoured pathway. This involves protonation of either the imido or amido ligand through a transient dihydrogen adduct and simultaneous hydride migration onto the tantalum centre (Figure 6). Together with the reverse reaction, α-hydrogen abstraction, these processes lead to complete exchange in the presence of the appropriate gas.[63]

The moderate activation barriers for the formation of these intermediates {for $[(\equiv SiO)_2Ta(NH_2)_2H]$, $\Delta E^\ddagger$ = 17.7 kcal mol^{-1} and $\Delta G^\ddagger$ = 26.7 kcal mol^{-1}; for $[(\equiv SiO)_2Ta(=NH)(NH_3)H]$, $\Delta E^\ddagger$ = 20.3 kcal mol^{-1} and $\Delta G^\ddagger$ = 30.2 kcal mol^{-1}} are consistent with the need for gentle heating to drive the reaction to completion. While calculations show that the dihydrogen adduct $[(\equiv SiO)_2Ta(=NH)(NH_2)(H_2)]$ is not an intermediate in the reaction, its appearance as a transition state in heterolytic H_2 splitting suggests that it adduct is relevant as a proton source for the ligated amido and imido moieties.

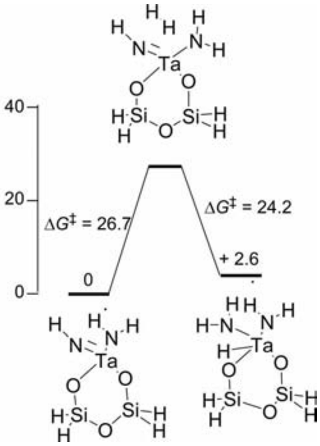
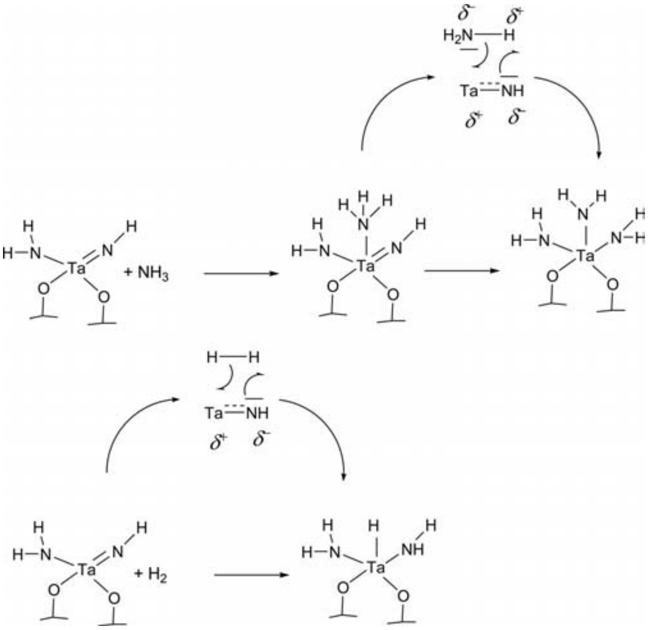


Figure 6. Calculated energies for the formation of the bis(amido) hydride from the imido amido species through a transient dihydrogen adduct.

The imido amido species **3** also heterolytically splits ammonia N–H bonds, induces H/D scrambling between NH_3 and ND_3 and $^{15}N/^{14}N$ exchange between $^{15}NH_3$ and NH_3.[64] Investigation by DFT shows an accessible route through heterolytic splitting of N–H bonds of ammonia across Ta=NH and Ta–NH_2. Alternative pathways for the exchange reaction were also considered computationally; intramolecular $TaNH_2$-to-TaNH H-transfer in $[(\equiv SiO)_2Ta(=NH)(NH_2)]$ has a prohibitively high activation barrier, and oxidative addition of H_2 onto the formally d^0 Ta^V centre is unlikely.[63] In the heterolytic activation of ammonia, the tantalum centre acts as a Lewis acid and the imido or amido moiety as the Lewis basic cooperating ligand (Scheme 4). Such cooperative tandem or bifunctional activation[65,66] through the Lewis acid/Lewis base couple formed by a metal centre and a ligated nitrogen atom,



Scheme 4. Ammonia N–H and dihydrogen H–H activation by $[(\equiv SiO)_2Ta(NH)(NH_2)]$ (**3**) with the bifunctional role of the Ta–N bond highlighted in heterolytic splitting, also called tandem cooperative activation.

termed "1,2-NH bond addition" or the "NH effect",[67] has already been highlighted in the heterolytic splitting of H_2[68] and is crucial to catalytic systems such as asymmetric hydrogenation of ketones.[69,70] The silica-grafted system $[(\equiv SiO)_2Ta(=NH)(NH_2)]$, for which we have already reported Ta=NH bifunctional activation of H_2, would be one of the few well-established examples of such an "NH effect" for ammonia activation.[50,59,71]

Such bifunctional activation, in which two functionalities cooperate in substrate activation and transformation, also appears relevant in the mechanism of formation of $[(\equiv SiO)_2Ta(NH)(NH_2)]$ from dinitrogen. Mechanistically, the cleavage of the N≡N triple bond by **2** is very surprising: multimetallic cooperation for N_2 cleavage has been reported in almost all previous literature,[72–78] including the Haber–Bosch catalyst[62] and the biochemical nitrogenase enzymes[79] (see Figure 7 for some selected representative examples); the only exception, besides our surface organometallic system, is the Yandulov–Schrock homogeneous catalyst, $[(HIPTN)_3N]Mo(N_2)$ {HIPT = 3,5-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$-C$_6$H$_3$NCH$_2$CH$_2$}.[80] While this latter system requires alternate addition of protons and reducing agents to achieve N_2 cleavage, the surface tantalum hydrides, $[(\equiv SiO)_2TaH]$ and $[(\equiv SiO)_2TaH_3]$, require only H_2. The mechanism by which this unique reactivity occurs has been investigated.[81]

Dihydrogen adducts, whether they occur as intermediates or transition states *en route* to heterolytic splitting, are involved in our silica grafted system.[82] Such involvement of H_2 on a classical heterogeneous catalyst, which generally contains multimetallic active sites, is not possible due to barrierless H_2 homolytic cleavage. On surfaces, dihydrogen adducts can only be found on isolated metal atoms: this is the case, for example, in Cu-doped zeolites,[83] where an $[(AlO_2)Cu(H_2)]$ adduct has been observed. Our SOMC products are a system on which the H_2 adduct can exist and can also perform chemistry previously unobserved in either homogeneous or heterogeneous catalysis. One of the reasons for the success of SOMC could therefore be that it combines (1) isolated metals displaying a well-defined first coordination sphere, as in solution chemistry, and (2) high working temperatures that open a pathway to processes with high activation barriers, as in heterogeneous catalysis. This unique reactivity may form the basis for using N_2 as a starting point for the formation of C–N bonds.

6. Conclusions

The highly electrophilic silica-supported tantalum hydrides $[(\equiv SiO)_2TaH]$ and $[(\equiv SiO)_2TaH_3]$ exhibit a distinct reactivity towards substrates typically considered difficult to activate, that is, alkanes (methane in particular) and dinitrogen. The rationale for this unique reactivity resides partly in the uniqueness of the SOMC approach for the synthesis of the starting materials. The SOMC approach allows the grafting of isolated organometallic centres on a silica support, which display the most notable characteristics of this system: (1) well-defined, (2) highly electrophilic, and

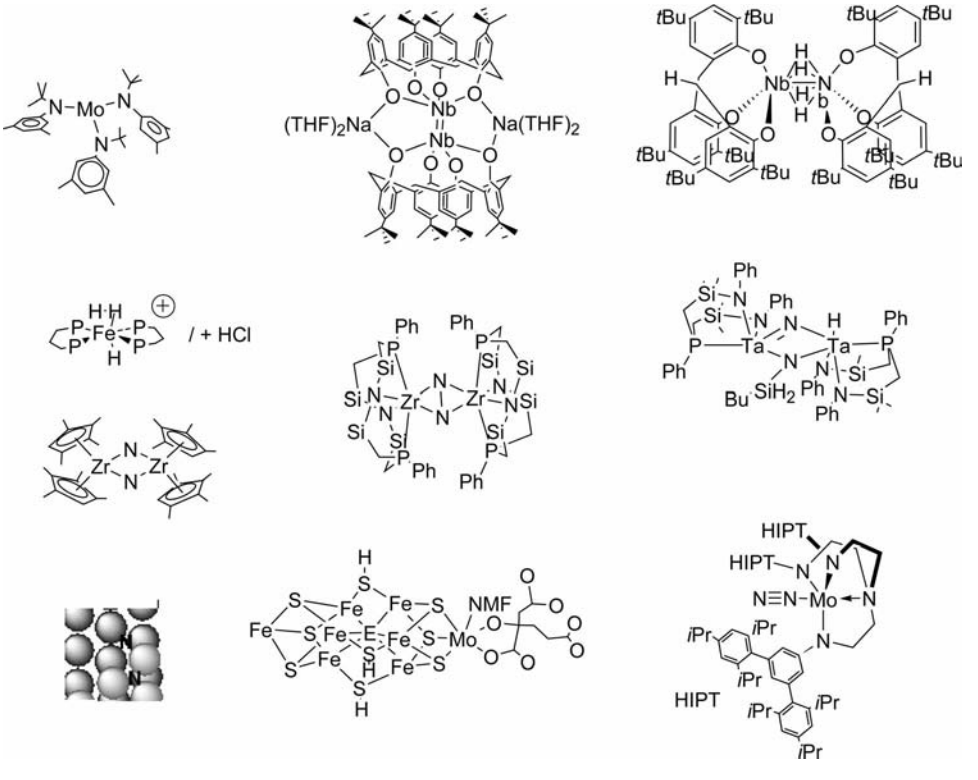


Figure 7. Systems able to cleave N_2: all[62,72–79] but one[80] are multimetallic, and only several are able to use H_2 as reducing agent.

(3) thermally robust metal centres. For example, the mild initial conditions, which are sufficient to ensure the grafting of the organometallic precursor {i.e., below 80 °C for Ta[=CH-*t*Bu(CH$_2$-*t*Bu)$_3$]}, lead to site isolation. Such site isolation could not be achieved at higher temperatures because of the higher thermal mobility of the species on the surface. Such mild grafting leads to robust and inert metal–oxygen bonds, which protect the metal hydride from common decomposition routes such as dimerization or sintering, the M–M bond-forming reaction that can occur in both homogeneous and classical heterogeneous systems obtained by impregnation. This site isolation secured through robust and inert M–O bonds to the surface is preserved during the subsequent hydrogenolysis step at higher temperatures, typically 150 °C, which gives rise to very electrophilic and reactive isolated hydrides [(surface-)MH$_x$] that are not prone to sintering. This behaviour stands in stark contrast to hydrogenolysis experiments performed on classical heterogeneous systems, which lead to metal aggregates with surface M–H$_x$ bonds and M–M bonds. Finally, the sturdy inorganic nature of the system with neither fragile organic side ligands, which are present in the classical heterogenization approaches, nor low-boiling solvents, present in homogeneous catalysis conditions, allow these kinetically locked isolated metal hydrides to sustain high reaction temperatures typical of heterogeneous catalysis.

Surface organometallic catalysts are thus able to catalyze or undergo stoichiometric reactions with high activation barriers, uncommon for regular molecular (whether homogeneous or supported) chemistry. In summary, the SOMC approach allows the synthesis of systems that can work under heterogeneous catalysis conditions and yet preserve the molecular site isolation and, to a certain extent, molecular environment, of homogeneous systems.

Due to the characteristics outlined above, tantalum hydrides **2**, [(≡SiO)$_2$TaH] and [(≡SiO)$_2$TaH$_3$], developed by the SOMC approach, have proven active in reactions with alkanes, catalyzing reactions such as alkane metathesis and non-oxidative coupling of methane. The importance of such reactivity is linked to increasing the value of abundant, yet unreactive, light alkanes. Elucidating the mechanism of alkane metathesis has proven the versatility of the tantalum hydrides: they act as (de)hydrogenation and olefin metathesis catalysts to yield alkane metathesis as the net transformation.

Cleavage of the N–H bond of ammonia and the N≡N triple bond of dinitrogen has also been achieved with the same starting hydrides. N$_2$ cleavage occurs in an unprecedented manner: on a monometallic site with H$_2$ as a reducing agent. Such chemistry on N$_2$ and NH$_3$ has highlighted two more unique properties ensured by the SOMC approach in addition to its previously mentioned advantages. First, the capacity of isolated tantalum atoms developed by SOMC to form dihydrogen adducts (unusual on surface systems) allows for the possibility of catalytic heterolytic cleavage; and secondly, the cooperative tandem or bifunctional activation that Ta–NH and Ta–H bonds can establish with H–H and N–H bonds, which is the key to substrate activation. These novel insights are being currently explored for N-based activation reactions with the eventual possibility of catalytic applications.

Acknowledgments

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