substituent intact. Conventional homometallic bases would conversely be expected to attack the latter group to generate resonance-stabilized benzyl carbanions.[11] Presumably operating through a special ring templating effect,[12] the active base(s) involved in the formation of **2** and **3** is a product of the heterodimetallic synergism taking place within the reaction mixture. In this respect, a parallel can be drawn with the chemistry of LiR · KOR′ superbases,[13] the mixed-metal reagents frequently utilized by synthetic organic chemists. More than thirty years since the first such application of superbases,[14] their mechanistic intricacies still remain to be fully unravelled, although it is established that the participation of the two distinct metal atoms is essential to the enhanced performance of superbases over that of analogous homometallic bases. Logic dictates that the mixed-metal templating ring involved in the formation of **2** and **3** must be larger and have more breadth than its counterpart in **II** given that only one end of the arene molecule experiences deprotonation, implying that the "other end" lies distant from a metal center.

Experimental Section

2 or **3**: Preparations were carried out in Schlenk tubes under a protective atmosphere of dry, oxygen-free argon. Freshly prepared but unrefined *n*BuK (15.1 or 12.3 mmol) was suspended in hexane (30 mL) and subjected to ultrasound for 5 minutes until a fine brown suspension formed. To this was added an equimolar amount of dibutylmagnesium (15.1 or 12.3 mmol, in heptane) resulting in the formation of a congealed brown/cream mass. Three molar equivalents of 2,2,6,6-tetramethylpiperidine (45.3 or 36.9 mmol) were then added. A slightly exothermic reaction ensued as most of the solid dissolved in the solvent mixture. Fine particulates were removed by filtration through Celite and the orange-brown filtrate was concentrated in vacuo to half of its original volume. At this stage 15 mL of the arene (**2**: benzene; **3**: toluene) was introduced and the solution was heated to 60°C and surrounded by a Dewar water bath. The solution cooled slowly over several hours to deposit rodlike orange/brown (**2**) or yellow (**3**) crystals. Yields **2**: 72.2 %; **3**: 80.5 %. Satisfactory C,H,N elemental analyses were obtained for both compounds. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C, TMS): **2**: $\delta = 7.94$ (m, 2H, *o*-C_6H_5), 7.31 (s, free C_6H_6), 6.87 (m, 2H, *m*-C_6H_5), 6.72 (m, 1H, *p*-C_6H_5), 1.68 (m, 2H, α-H), 1.25 (m, 4H, β-H), 1.06 (s, 12H, γ-H; **3**: $\delta = 7.83$–7.65 (m, 2H, bound $C_6H_4CH_3$), 7.18–7.10 (m, free $C_6H_5CH_3$), 6.75–6.63 (m, 1H, bound $C_6H_4CH_3$), 6.08 (m, 1H, bound $C_6H_4CH_3$), 2.30 (s, free $C_6H_5CH_3$), 2.16 (s, 3H, bound $C_6H_4CH_3$), 1.65 (m, 2H, α-H), 1.25 (m, 4H, β-H) and 1.09 (s, 12H, γ-H); ^{13}C NMR (75 MHz, [D$_8$]THF, 25 °C, TMS): **2**: $\delta = 181.57$ (*ipso*-C_6H_5), 142.28 (*o*-C_6H_5), 128.84 (free C_6H_6), 125.10 (*m*-C_6H_5), 122.61 (*p*-C_6H_5), 52.90 (tmp γ-C), 42.47 (tmp α-C), 36.13 (tmp β-C), 21.62 (tmp Me); **3**: $\delta = 158.64$ (bound $C_6H_4CH_3$), 143.56 (bound $C_6H_4CH_3$), 142.13 (bound $C_6H_4CH_3$), 137.94 (free $C_6H_5CH_3$), 129.48 (free $C_6H_5CH_3$), 128.71 (free $C_6H_5CH_3$), 127.61 (bound $C_6H_4CH_3$), 125.70 (free $C_6H_5CH_3$), 123.10 (bound $C_6H_4CH_3$), 112.63 (bound $C_6H_4CH_3$), 52.75 (tmp γ-C), 42.44 (tmp α-C), 36.11 (tmp β-C), 24.64 (free $C_6H_5CH_3$), 21.14 (tmp Me), 19.98 (bound $C_6H_4CH_3$).

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Low-Temperature Hydrogenolysis of Alkanes Catalyzed by a Silica-Supported Tantalum Hydride Complex, and Evidence for a Mechanistic Switch from Group IV to Group V Metal Surface Hydride Complexes[**]

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We report herein a low-temperature hydrogenolysis of alkanes on a silica-supported tantalum hydride and the striking difference in reactivity compared to similar reactions

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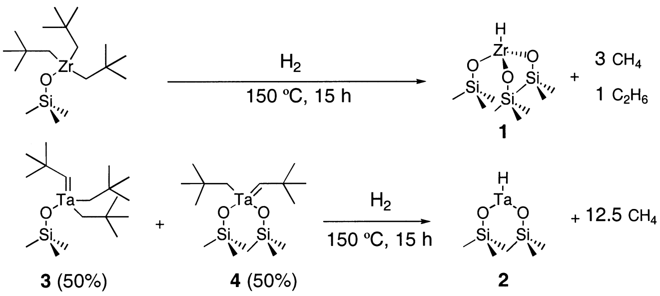
of silica-supported Group IV hydrides, for example in the hydrogenolysis of ethane.[1]

Our group has shown that the silica-supported Group IV metal hydrides **1**, $(\equiv SiO)_3M{-}H$ (M = Ti,[1c], Zr,[1a] or Hf[1b]), readily catalyze the hydrogenolysis of simple alkanes, such as propane, butanes, and pentanes (but with the exception of ethane), into mixtures of methane and ethane at low temperatures (25 to 150 °C). It even transforms polyethylene into lower molecular weight alkanes (all the way from diesels to mixtures of methane and ethane).[2] These catalytic reactions are readily explained by a mechanism which involves a β-alkyl transfer[3] as the key step for carbon–carbon bond cleavage. Interestingly, this elementary step corresponds to the microscopic reverse of insertion of an olefin into a metal–carbon bond, the carbon–carbon bond formation step (propagation) involved in Ziegler–Natta polymerization.[4]

The surface complex **1** is usually obtained by selective hydrogenolysis of $(\equiv SiO)M(Np)_3$ with molecular H_2 at 150 °C (Np = neopentyl). During this hydrogenolysis, there is formation of a 3:1 mixture of methane and ethane, a product distribution which is in agreement with the β-alkyl transfer mechanism (Scheme 1).[1a]

In sharp contrast to the behavior of group IV metal hydrides, the hydrogenolysis of the tantalum surface complexes **3** and/or **4** leads to the formation of methane as the only final product, thus showing a dramatic difference of reactivity (Scheme 1). This hydrogenolysis also yields a tantalum hydride complex $(\equiv SiO)_2Ta{-}H$, **2**, which is a remarkable catalyst for the metathesis of paraffins.[5, 6] We have been puzzled by the striking differences of behavior between **1** and **2** for the stoichiometric formation of the surface hydrides. This led us to further investigate the catalytic activity of **2** for the hydrogenolysis of various alkanes, including ethane.

In a glass batch reactor, a mixture of hydrogen and acyclic alkanes (C_nH_{2n+2}; $n > 1$) in the presence of **2** are typically converted into their lower homologues, that is, $C_{n-1}H_{2n}$ to CH_4, and only CH_4 is detected at full conversion (Figure 1). The product distribution is typical of successive cleavage of the carbon–carbon bonds, for example, the successive formation and disappearance of propane and ethane in the hydrogenolysis of 2-methylpropane. The product selectivity is constant at conversions of 50–80% (Table 1), depending on the starting material; these constant selectivities are consistent with the observation of primary products, and can therefore provide potential mechanistic information regarding the carbon–carbon bond cleavage step. Moreover, the observed selectivities at low conversions are quite informative. For example, a 50:50 mixture of ethane and methane could be expected at low conversion in the hydrogenolysis of propane, yet a 43:57 mixture is obtained at various temperatures, showing that ethane resulting from the C–C bond cleavage of propane is partially cleaved before being desorbed (Table 1, entry 2).



Scheme 1. The metals are attached to the silica suface by siloxy groups shown as ≡SiO.

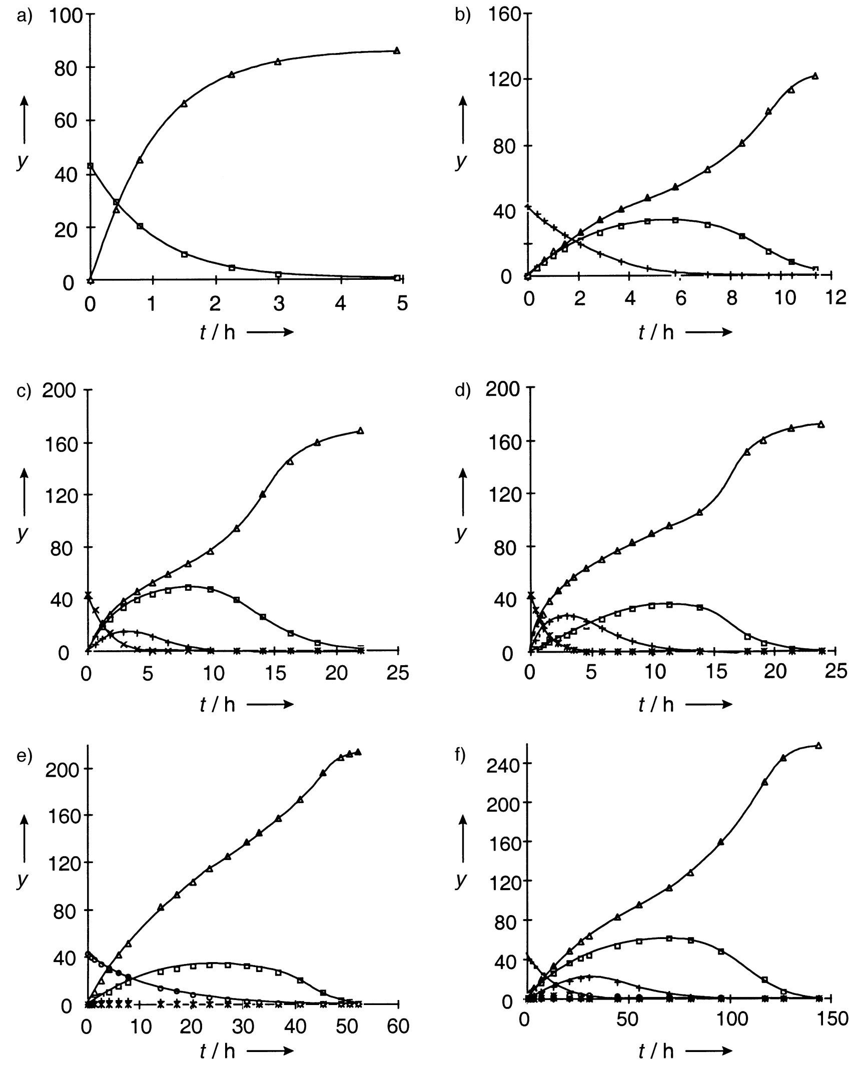


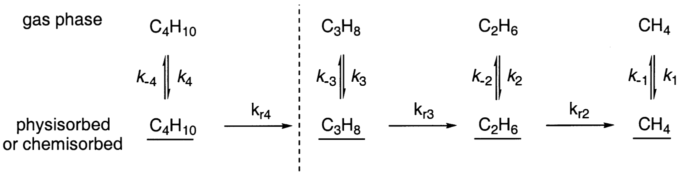
Figure 1. Hydrogenolysis of alkanes over a silica-supported tantalum hydride surface complex **2**. The *y* axis shows the equivalents of products formed relative to one equivalent of **2**. The *x* axis shows time in hours. a) Ethane hydrogenolysis; b) propane hydrogenolysis; c) butane hydrogenolysis; d) 2-methylpropane hydrogenolysis; e) neopentane hydrogenolysis; f) 2,2-dimethylbutane hydrogenolysis. △ = Methane, □ = ethane, + = propane, × = butane, * = 2-methylpropane, ○ = neopentane, - = 2,2-dimethylbutane.

Table 1. Initial rate constants (k) and selectivities at low conversions for the hydrogenolysis of alkanes over $(\equiv SiO)_2Ta{-}H$ at 160 °C.[a]

Entry	alkane	k [h^{-1}]	pentanes	butanes	propane	ethane	methane
1	ethane	1.0	–	–	–	–	100
2	propane	0.36	–	–	–	43 (50)	57 (50)
3	2-methylpropane	0.74	–	1.6[b]	35.2 (50)	9.2 (0)	53.9 (50)
4	butane	0.65	–	1.8[b]	19.5 (33)	36.3 (33)	42.4 (33)
5	Np-H	0.08	–	–[c]	–[c]	–[c]	–[c]
6	n-C_5H_{12}	0.33	2.2[d]	7.1[e] (25)	20.0 (25)	37.5 (25)	33.0 (25)
7	Np-Me	0.07	8.5[f,g] (10)	7.5[f,h] (10)	11.7 (0)	29.8 (10)	40.8 (40)

[a] The numbers in parenthesis correspond to the expected selectivities if the first carbon–carbon bond cleavage were statistical. [b] This corresponds to the selectivity in the other isomer. [c] Selectivies are not constant even at low conversion since neopentane reacts slower than the products formed. [d] Selectivity in 2-methylbutane. [e] Selectivity in butane; the selectivity in 2-methylpropane is 0.2 %. [f] The selectivities decrease slowly with conversion. [g] Selectivity in neopentane; the selectivities in 2-methylbutane and pentane are 1.0 % (30), and 0 % (0), respectively. [h] Selectivity in 2-methylpentane only, the selectivity in butane is 0.7 % (0).

The same observation applies to higher alkanes. In fact, it is even more dramatic in the case of 2-methylpropane in which the selectivity in propane is only 35 % compared with an expected 50 % (Table 1, entry 3). This shows that the process does not involve purely successive reactions and, also, that there is a greater probability for a higher alkane to react further rather than desorb (Scheme 2, physisorption and/or chemisorption).

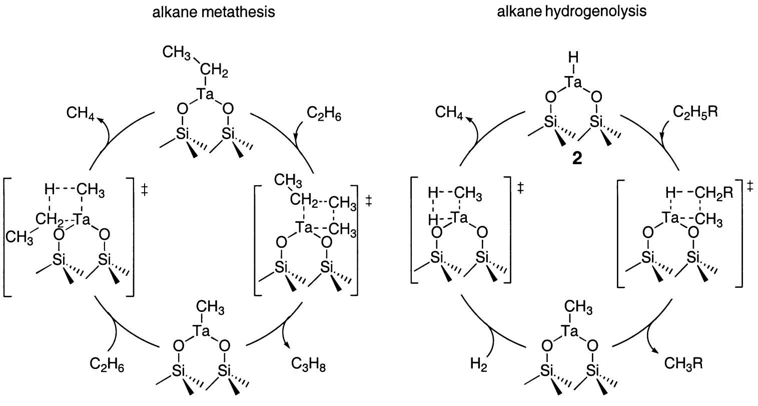


Scheme 2.

Three molecules deserve a special interest. Firstly, ethane is catalytically cleaved by **2** into methane (Table 1, entry 1), which obviously cannot be explained by a β-alkyl transfer mechanism since the corresponding ethyl–tantalum surface complex, $(\equiv SiO)_2Ta{-}CH_2CH_3$, does not have an alkyl group in the β-position. This shows that a one-carbon transfer process is possible with this catalyst, in contrast to what has been observed for Group IV metals (see above). However, it is difficult to discriminate between one- or two-atom transfer processes (like β-alkyl transfer) for simple linear or branched alkanes such as butane or 2-methylpropane. This led us to investigate the hydrogenolysis of 2,2-dimethylbutane (Np-Me, Table 1, entry 7). Under identical conditions, this molecule gave neopentane as the major product of higher alkanes (> C_3). In this case, neopentane cannot be produced by a β-alkyl transfer, which clearly shows that another process for carbon–carbon bond cleavage takes place even for higher alkanes. Finally, in the case of neopentane (Np-H, Table 1, entry 5), there is no build-up of intermediary products (like 2-methylpropane or propane), thus showing its slower reactivity relative to the lighter alkanes formed during its hydrogenolysis. This is in contrast to what has been observed for other alkanes including pentane (see above) and also for its hydrogenolysis in the presence of **1**.[1a, 7] This is probably due to steric reasons and also suggests that the actual carbon–carbon bond cleavage step might also be different from a β-alkyl transfer.

In the light of the specific abilities of tantalum hydride to also catalyze alkane metathesis,[6] which transforms an alkane into its higher and lower homologues, we suggest that the mechanism for carbon–carbon bond cleavage could be closely related to that of alkane metathesis. The key step of the proposed mechanism involves the formation and cleavage of a carbon–carbon bond by interaction of an alkane molecule with a tantalum–carbon bond by σ-bond metathesis (Scheme 3). In the case of the hydrogenolysis of ethane (R = H), the interaction of the Ta–H bond directly with a carbon–carbon bond, via a four-centered transition state, leads to methane and a Ta–Me surface species; the latter, which can readily give methane through a related σ-bond metathesis mechanism under H_2, is regenerated into the catalyst, **2**.[8] The same mechanism can be also extended to higher alkanes in the case of tantalum (see above, for example, neopentane and 2,2-dimethylbutane). This is dramatically different from group IV metals in which β-alkyl transfer is the only carbon–carbon bond cleavage process.

In conclusion, the tantalum hydride **2** catalyzes the low-temperature hydrogenolysis of alkanes, including that of ethane, in sharp contrast with Group IV metal hydrides. This surface complex also catalyzes alkane metathesis, while surface complexes like **1** do not. We are currently further investigating these two reactions.



Scheme 3. The tantalum is attached to the silica suface by siloxy groups shown as ≡SiO.

Experimental Section

The reactions were carried out with the same batch of catalyst in the absence of oxygen and water under the following conditions: $(\equiv SiO)_2Ta{-}H$ (prepared by impregnation, 18.8×10^{-6} mol of Ta, 1 equiv), alkane (40 Torr, 43 equiv), and H_2 (630 Torr, 710 equiv) were heated with an oil bath to the desired temperature ($\pm 1\,^{\circ}C$) in a glass batch reactor (376 mL). During the reaction, aliquots were expended, brought to atmospheric pressure, and analyzed by gas chromatography (HP 5890 apparatus, Al_2O_3/KCl on fused silica column, 50m × 0.32mm). Alkanes and H_2 were dried over freshly regenerated molecular sieves (3Å) and deoxo traps before addition.

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Unprecedented Formation of Five-, Six-, and Seven-Membered Metallacycles by Single and Double Insertion of Mono- and Disubstituted Alkynes into an Rh–O Bond**

Yasuhiro Yamamoto,* Xiao-Hong Han, and Jian-Fang Ma

Metal alkynyl complexes are currently of great interest[1, 2] since they are valuable for constructing vinylidene or carbene complexes for use in organic synthesis.[3–8] Reactions of organotransition metal halides with 1-alkynes in the presence of anions such as PF_6^-, BF_4^-, and $CF_3SO_3^-$ are representative methods for the preparation of vinylidene complexes.[9] One *ortho*-methoxy group in (2,6-dimethoxyphenyl)diphenylphosphane (mdmpp) was demethylated in the reaction with the isoelectronic complexes $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = C_6Me_6, *p*-cymene, $C_6H_3Me_3$) and $[Cp^*MCl_2]_2$ (M = Rh, Ir) to give metal complexes with a (*P,O*)-chelating phosphane: $[(\eta^6\text{-arene})RuCl(\text{mdmpp-}\kappa P,\kappa O)]$[10, 11] and $[Cp^*MCl(\text{mdmpp-}\kappa P,\kappa O)]$[12, 13] ($Cp^* = C_5Me_5$). We recently reported the unprecedented insertion of tetracyanoethylene (tcne) and tetracyanoquinodimethane into the C–H bond adjacent to the M–O bonds of the above rhodium(III) and iridium(III) complexes to produce (*P,O*)-chelated $[Cp^*MCl[PPh_2\{2\text{-}O\text{-}6\text{-}MeO\text{-}3\text{-}(CH(CN)_2C(CN)_2)C_6H_2\}]$ in the case of tcne.[14]

Treatment of the ruthenium(III) complex with $PhC\equiv CH$ in the presence of $NaPF_6$ in acetone/CH_2Cl_2 afforded the vinylidene complex $[(\eta^6\text{-arene})Ru(\text{mdmpp-}\kappa P,\kappa O)(=C=CHPh)]PF_6$.[15] However, treatment of $[Cp^*RhCl(\text{mdmpp-}\kappa P,\kappa O)]$ (**1**)[12] with 1-alkynes such as $HC\equiv CCOOMe$, $PhC\equiv CH$, and $n BuC\equiv CH$, and the disubstituted alkyne $C_2(CO_2Et)_2$ in the presence of $NaPF_6$ or KPF_6 resulted in unusual reactions (Scheme 1). In the reaction with $HC\equiv CCOOMe$, extraction of CO from the ester group of one and insertion of another 1-alkyne molecule into the Rh–O σ bond occurred to produce a seven-membered metallacycle, and reactions with $HC\equiv CR$ led to the formation of complexes with five- and six-membered rings by double insertion of 1-alkynes into the Rh–O bond. The disubstituted alkyne also underwent single insertion into the Rh–O bond. Similar insertion of unsaturated molecules into the metal–oxygen bonds of metal alkoxides was achieved with cyclooctadiene[16] and perfluoroolefins[17] such as $F_2C{=}CF_2$ and hexafluorocyclobutene. The insertion of alkynes into the transition metal to oxygen σ bonds was achieved here for the first time.[18] Interestingly, these unprecedented reactions allow single and double insertion of alkynes into the Rh–O bond of **1** to be controlled by means of the alkyne substituents.

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