

# Mechanistic Investigations of C–H Activations on Silica-Supported Co(II) Sites in Catalytic Propane Dehydrogenation

Deven P. Estes<sup>§\*</sup>

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**Abstract:** Catalytic reactions involving C–H bond activations are central to the chemical industry. One such example, alkane dehydrogenation, has recently become very important due to shortfalls in propene production and a large supply of cheap propane. However, current technologies are inefficient and have only moderate selectivity. In order to understand how to improve currently used catalysts, we must know more about the mechanism by which propane is dehydrogenated. We show here that Co(II) sites on silica are good catalysts for the dehydrogenation of propane, having high activity and selectivity that is reasonably stable over the course of 10 h. Mechanistic investigations of this catalyst show that the main activation mechanism is most likely C–H activation by 1,2 addition.

**Keywords:** C–H activation · Surface Organometallic Chemistry (SOMC)



*Deven Estes received a B.S. in chemistry from the University of Oklahoma in 2009. In 2014 he earned his PhD from Columbia University, where he was a Department of Energy Predoctoral Fellow in the laboratory of Prof. Jack Norton. In 2014, he moved to ETH Zürich, where he was a Marie Curie Postdoctoral Fellow in the Laboratory of Prof. C. Copéret. He is currently a postdoctoral researcher at RWTH Aachen in the laboratory of Prof. Walter Leitner where he will conduct research on heterogeneous catalysts for CO<sub>2</sub> conversion.*

## Introduction

A large number of chemical and petrochemical processes rely on heterogeneous catalysts to carry out the desired transformation. Many of these processes, including hydrocracking, alkane dehydrogenations, and possibly even olefin polymerizations,<sup>[1]</sup> involve C–H activation at some point in the catalytic cycle to carry out the desired reaction. In addition, C–H activation is often the rate determining step in these reactions and, thus, in order to improve the performance of the current state of the art catalysts used in industry, we need to understand more about how C–H activations on these catalysts happen.

One such reaction is the dehydrogenation of light alkanes, such as ethane and propane, that have recently become central to the petrochemical processes. This resurgence of interest is due to rising propene demand, falling propene production, and large amounts of cheap propane obtained from shale gas.<sup>[1d]</sup> However, alkane dehydrogenation is a challenging reaction for a variety of reasons. For one, it is highly endothermic, meaning it must be performed at high temperatures (550–750 °C) in order to obtain high equilibrium concentrations (Scheme 1, reaction (1)). Secondly, at these temperatures coke formation (reaction (2)) and cracking (reaction (3)) are in competition with the desired dehydrogenation reaction, lowering the yield. A good catalyst for the reaction

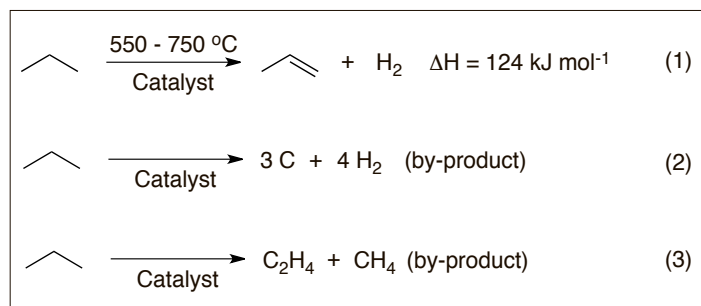
must be stable to the high temperatures necessary for reaction and must be very selective to avoid coke formation and to give optimal yield.

The current catalysts for propane dehydrogenation are inefficient (due to their need for frequent reactivation, *vide infra*) and have only moderate selectivity.<sup>[2]</sup> One such catalyst consists of CrO<sub>3</sub> dispersed on alumina and is synthesized through impregnation of silica with CrO<sub>3</sub> in water followed by calcination under flow of synthetic air at 500 °C.<sup>[3]</sup> This catalyst gives propene with 89% selectivity. However, due to coke formation the catalyst deactivates after only seven minutes on stream.<sup>[1d,4]</sup> Thus, every seven minutes, the catalyst must be regenerated through a calcination step in order to remove the coke from the surface. Therefore, finding an alternative catalyst with better properties, in particular stability, would be advantageous.

Hock and coworkers have shown that when [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> in aqueous solution is adsorbed onto silica at high pH (9–10) and then calcined, the result is Co(II) sites dispersed across the surface of silica.<sup>[5]</sup> They reported that while this catalyst has rather low activity for propane dehydrogenation, it produces propene with up to 95% selectivity with very little coke formation. If the activity of this catalyst could be improved, then this would represent a significant improvement to the current state of the art and would go a long way toward improving the efficiency of this process.

\*Correspondence: Dr. D. P. Estes  
ETH Zürich  
Department of Chemistry and Applied Biosciences  
Vladimir-Prelog-Weg 1–5, CH-8093 Zürich  
E-mail: destes@inorg.chem.ethz.ch

Scheme 1. Alkane dehydrogenation.



The rate of propane dehydrogenation on heterogeneous catalysts like these is thought to be controlled by the rate of C–H activation. Thus, before improving the catalyst, we must understand how to increase the rate of C–H activation. This requires knowledge of the mechanism of the reaction. However, the mechanism of C–H activation on these catalysts is unknown due to the difficulty of studying reaction mechanisms on heterogeneous surfaces. For instance, heterogeneous catalysts often have a very low percentage of active sites on the surface (<10%), which makes it difficult to understand the structure of the active sites.<sup>[6]</sup> We need a better synthetic method in order to have a higher percentage of active sites, so that we may study the structure of the active sites. We can then use this material for mechanistic investigations of various C–H bond activation processes.

We have shown previously that Surface Organometallic Chemistry (SOMC)<sup>[7]</sup> combined with the thermolytic molecular precursor (TMP)<sup>[8]</sup> approach allows the synthesis of transition-metal sites on silica surfaces in a controlled way.<sup>[1b,c,e,9]</sup> This involves using silica dehydroxylated at 700 °C (SiO<sub>2-700</sub>) having chemically equivalent SiOH groups statistically spaced (~1 nm apart) on the surface. Reacting metal complexes having basic ligands with this material results in release of the ligand plus a metal surface bond (Fig. 1). If the metal complex is ligated by tris-tert-butoxysiloxide ((tBuO)<sub>3</sub>SiO– or TBOSO–) as in TMP, the grafted species can be treated under vacuum at high temperature (300–500 °C) to lose all the organic fragments, resulting in a material that is only ligated by the silica surface itself. The materials so synthesized have properties and reactivity that mimic those of the industrial catalysts after which they are modeled.<sup>[1b,c,e]</sup> We showed that grafting Cr precursors by this method resulted in a material that had very similar reactivity to the Phillips catalyst for ethylene polymerization.<sup>[1b,c]</sup> However, unlike its industrial counterpart, this new material with Cr had 60% active sites on the surface. We also showed that this material is active for propane dehydrogenation, meaning that these catalysts are stable up to the harsh conditions of the reaction.<sup>[1c]</sup> Thus, we

opted for the same strategy to make well-defined Co sites on the surface and study their reactivity toward C–H bonds.

As outlined in our recent paper,<sup>[10]</sup> we synthesized the dimeric Co<sub>2</sub>(OTBOS)<sub>4</sub> (**1**) molecular precursor by reaction of 2 equiv. TBOSOH with Co(HMDS)<sub>2</sub>(THF).<sup>[11]</sup> The molecular structure is shown in Fig. 1 (top). Reaction of a green solution of **1** with SiO<sub>2-700</sub> produced a blue solid containing 0.28 mmol Co g<sup>-1</sup>, and released 1 equiv. of TBOSOH per surface Co. IR spectroscopy showed consumption of almost all the surface OH groups and new C–H stretching and bending bands. This grafted material (**2**) retained roughly one TBOS ligand per surface Co suggesting that monomeric Co centers were present on the surface. Heating of material **2** under high vacuum at 500 °C resulted in the complete loss of all alkyl groups from the surface and regenerated some surface silanols as seen in the IR spectrum (Fig. 1 (bottom)).

Characterization of the surface Co sites in materials **2** and **3** was carried out with a variety of techniques. The electronic spec-

tra of materials **2** and **3** were all similar and characteristic for high-spin tetrahedral Co(II) sites. The electronic spectra of **2** and **3** differed significantly from that of **1**, suggesting a change in coordination environment. However, all three of these materials were EPR silent even at 4 K, most likely due to fast relaxation due to coupling of the ground state with low lying excited electronic states.<sup>[12]</sup> We further confirmed the assignment of high-spin Co(II) through the use of X-ray absorption spectroscopy. The Co K-edge X-ray absorption near edge spectra (XANES) of **1–3** (Fig. 2) show that all materials have nearly the same pre-edge and edge energies and intensities, suggesting that they all have similar oxidation states and local structures. In addition, fitting the extended X-ray absorption fine structure (EXAFS) spectrum showed that each Co had, on average, four oxygen nearest neighbors, supporting the assignment of these structures as tetrahedral.

We also noticed in the EXAFS spectrum of **2** and **3** that there were unidentified peaks at longer distances most likely belonging to some heavier atom than oxygen. Attempts to determine the identity were inconclusive and close contacts between both Co–Co and Co–Si could plausibly explain this observation. In order to determine the identity of this nearby heavy atom, we turned to a technique known as Wavelet Analysis.<sup>[13]</sup> In traditional EXAFS, fitting a Fourier transform of the interference pattern (called k-space, a function of energy) creates a new plot called R-space (a function of distance). This allows the user to measure distances of nearest neighbor

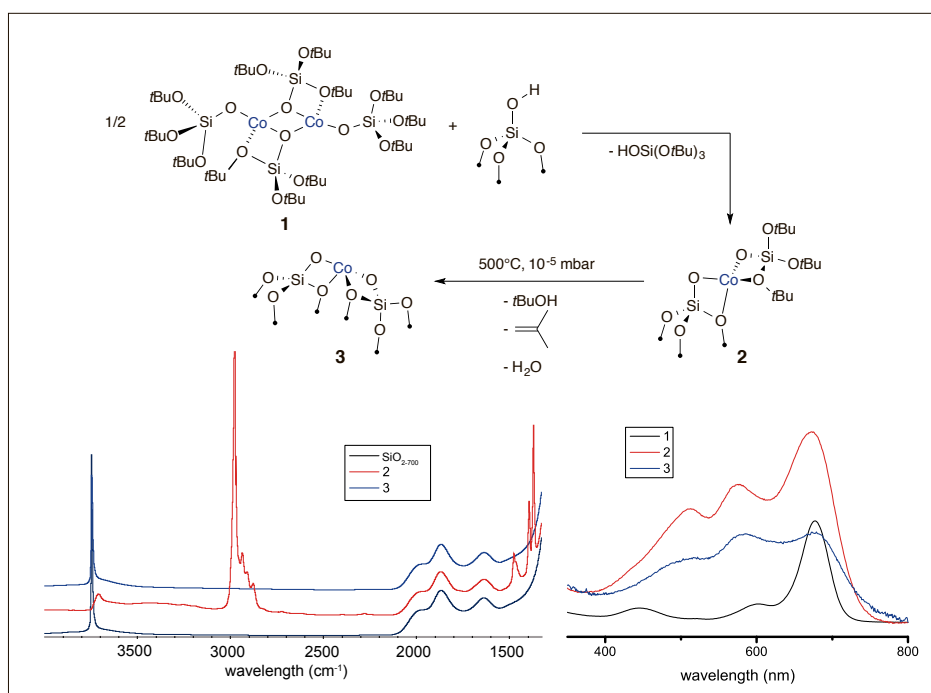


Fig. 1. Grafting of **1** on silica followed by thermal treatment as monitored by IR and UV-Vis spectroscopies.

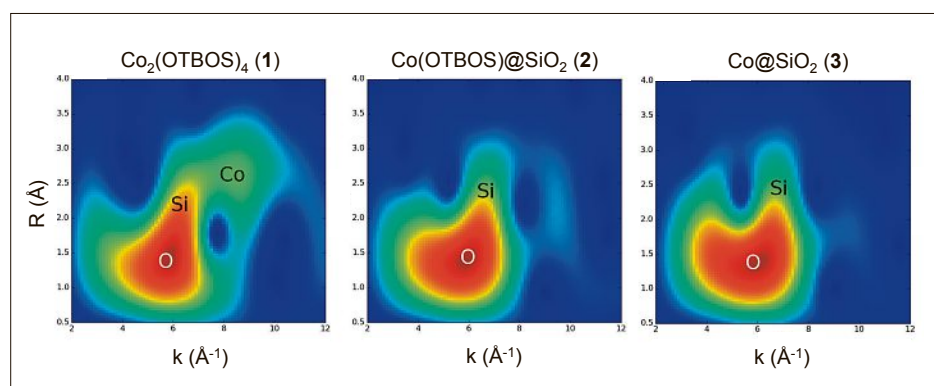


Fig. 2. Wavelet Analysis of EXAFS data of 1–3.

atoms from the excited atom. A wavelet transform is an alternative to a Fourier transform and creates a two-dimensional plot of  $k$ -space versus  $R$ -space. In this two-dimensional plot, cross peaks show how different sections of the interference pattern contribute to different intensities in the energy dimension. Thus, it is possible to identify the scattering partner of a specific peak in  $R$ -space by where its contribution to the interference pattern is in  $k$ -space. Our wavelet analysis shows that **1** has a strong cross peak at the correct position for Co–Co scattering paths. However, this peak is not present in **2** and **3**, supporting our assignment of these surface structures as monomeric. Thus, we can say confidently that **2** and **3** consist of monomeric high-spin tetrahedral Co(II).

Now that we had identified the structure of the Co(II) sites on the surface we tested the reactivity of these species toward C–H bond activation. We found that **3** was indeed a catalyst for the dehydrogenation of propane. The results are shown in Fig. 3. At 550 °C, **3** dehydrogenates propane to produce propene with a maximum selectivity of 89% and maximum turnover frequency of 12 h<sup>-1</sup>. The activity of the catalyst decayed to 5 h<sup>-1</sup> after 10 h on stream. However, the selectivity had the opposite trend. In the first hour of reaction the catalyst formed large amounts of coke, and as coke formation slowed the selectivity of the reaction rose until reaching a maximum point of 89% selectivity that slowly but steadily decreased until the end of the 10 h experiment. The catalyst recovered after the reaction consisted of 11–12 wt% C in the form of nanotubes and contained a broad distribution of Co nanoparticles that were created during catalysis.

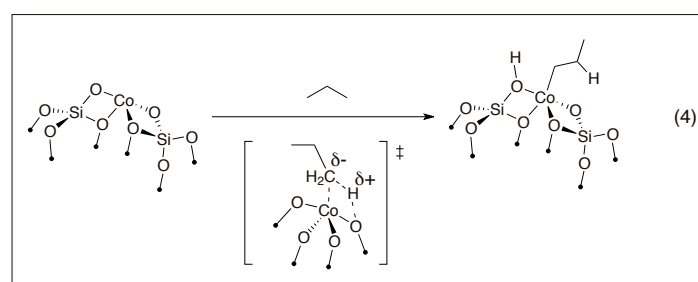
We now attempted to understand more about the mechanism of this process on material **3**. Due to the deactivation of the catalyst, kinetic measurements were not possible. However, we were able to glean some mechanistic information from other extra-kinetic probes. It is common for transition-metal complexes to activate

C–H bonds through C–H bond homolysis processes such as proton-coupled electron transfer (PCET) or hydrogen atom transfer (HAT).<sup>[14]</sup> However, it is also common for other mechanisms such as oxidative addition or 1,2-addition to be active. In order to test for the possibility that homolytic mechanisms are active, we compared the TOF of **3** for propane dehydrogenation with the TOF for isobutane dehydrogenation. If a homolytic mechanism were active, the tertiary C–H bond in isobutane should react about twice as fast as a secondary C–H bond in propane at 550 °C.<sup>[15]</sup> However, since there are two secondary C–H bonds in propane and only one tertiary C–H bond in isobutane, the TOF of isobutane dehydrogenation and propane dehydrogenation would be equal if a homolytic mechanism was active. However,

mechanisms like oxidative addition and 1,2-addition are selective for primary C–H bonds.<sup>[16]</sup> Thus, if a heterolytic mechanism were active we would expect that the ratio of the TOFs for the two reactions would be proportional to the number of primary C–H bonds in each molecule, roughly 1.7. When we measured the initial TOF for isobutane dehydrogenation we found that it was 1.6 times higher than that of propane at 550 °C, suggesting that a mechanism like oxidative addition or 1,2-addition is active (Scheme 2).

Distinguishing between oxidative addition and 1,2-addition mechanisms has been more difficult. Oxidative addition usually requires a low-coordinate electron-rich metal center and metal centers that do C–H bond oxidative addition are usually very reactive toward oxidants. However, catalyst **3** is not reactive toward common oxidants such as I<sub>2</sub> and O<sub>2</sub>. In contrast, 1,2-addition requires that metal centers be quite Lewis acidic. Our catalyst does indeed bind Lewis bases such as water, THF, and CO. Furthermore, the CO stretching frequency of CO bound to **3** is blue shifted with respect to free CO (2184 cm<sup>-1</sup>). This suggests that the main bonding interaction of CO to the Co sites on the surface is Lewis acidic/basic in nature with no or very little  $\pi$ -backbonding from the metal to CO.<sup>[17]</sup> This all suggests that the main C–H activation mechanism is 1,2-addition and not oxidative addition.

In order to take a closer look at the mechanism, we decided to investigate the



Scheme 2. C–H bond activation on Co surface sites by a 1,2-addition type mechanism.

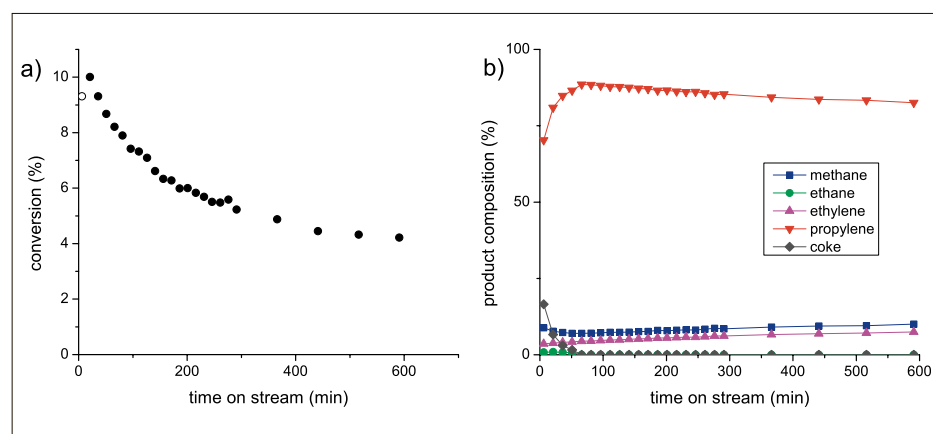
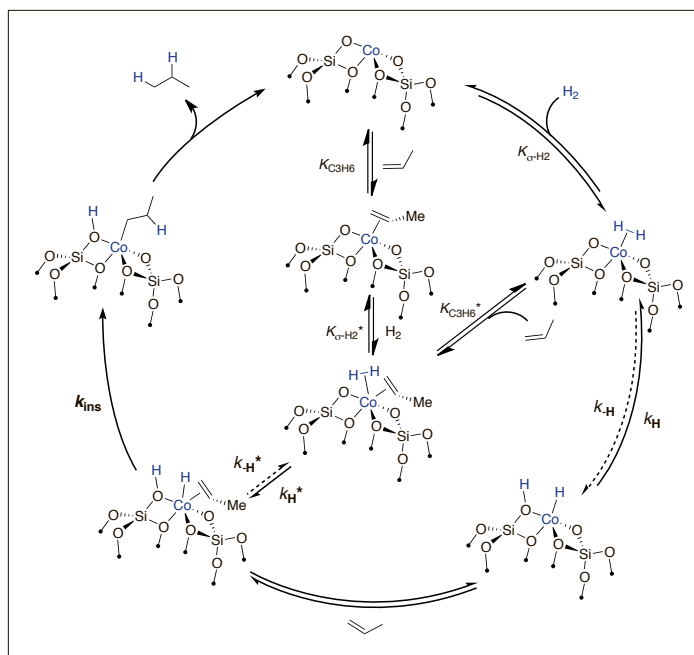


Fig. 3. a) Conversion and b) product composition from reaction of **3** with propane as a function of time on stream.

reverse reaction, namely the hydrogenation of propene catalyzed by **3**. We found that hydrogenation was catalyzed by **3** at temperatures as low as 50 °C without deactivation of the catalyst. We found that the rate law of the reaction was first order in  $H_2$  pressure and showed saturation behavior in propene pressure. Changing from  $H_2$  to  $D_2$  gave an isotope effect that was temperature dependent and varied from 1 to 2.7 but approached 1 at high temperature. When para-hydrogen was substituted for ortho-hydrogen, as in a para-hydrogen induced polarization (PHIP) experiment,<sup>[18]</sup> polarization transfer was observed from  $H_2$  to propane. This means that both H atoms in a new product propane molecule came from the same molecule of  $H_2$ . All of this suggested a mechanism similar to what we had proposed for propane dehydrogenation. This mechanism involves pre-equilibrium binding of both  $H_2$  and propene to the active site, followed by splitting of  $H_2$  and insertion of propane (Scheme 3). If this happens by a 1,2 addition, that means that this mechanism is the microscopic reverse of the one shown above for dehydrogenation.

We have shown that the catalyst **3** is a selective catalyst for the dehydrogenation of alkanes like propane, consistent with previous reports. We have also shown that this catalyst does so with relatively high activity. Mechanistic studies of this catalyst suggest that the rate-determining step of the reaction is C–H activation, which probably goes through a 1,2 addition type mechanism.<sup>[1a,19a,b]</sup> The same type of mechanism was also observed for methane activation by low coordinate aluminum sites on alumina surfaces.<sup>[20]</sup> This mechanism is consistent with the Lewis acidic character of the active site. We were able to rule out several other mechanisms, such as radical based H atom abstractions. Future work will go toward increasing the stability of this catalyst under reaction conditions.

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Scheme 3. Proposed mechanism of propene hydrogenation and microscopic reverse mechanism of propane dehydrogenation.

- [1] a) C. Copéret, *Chem. Rev.* **2010**, *110*, 656; b) M. P. Conley, M. F. Delley, G. Siddiqi, G. Lapadula, S. Norsic, V. Monteil, O. V. Safonova, C. Copéret, *Angew. Chem. Int. Ed.* **2014**, *53*, 1872; c) M. F. Delley, F. Núñez-Zarur, M. P. Conley, A. Comas-Vives, G. Siddiqi, S. Norsic, V. Monteil, O. V. Safonova, C. Copéret, *Inorg. Chem.* **2015**, *54*, 5065; f) E. T. C. Vogt, B. M. Weckhuysen, *Chem. Soc. Rev.* **2015**, *44*, 7342.
- [2] H. Zimmermann, in 'Ullmann's Encyclopedia of Industrial Chemistry', Wiley-VCH Verlag GmbH & Co. KGaA, **2000**.
- [3] B. M. Weckhuysen, I. E. Wachs, R. A. Schoonheydt, *Chem. Rev.* **1996**, *96*, 3327.
- [4] J. J. H. B. Sattler, I. D. Gonzalez-Jimenez, L. Luo, B. A. Stears, A. Malek, D. G. Barton, B. A. Kilos, M. P. Kaminsky, T. W. G. M. Verhoeven, E. J. Koers, M. Baldus, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2014**, *53*, 9251.
- [5] B. Hu, A. Getsoian, N. M. Schweitzer, U. Das, H. Kim, J. Niklas, O. Poluektov, L. A. Curtiss, P. C. Stair, J. T. Miller, A. S. Hock, *J. Catal.* **2015**, *322*, 24.
- [6] M. P. McDaniel, S. J. Martin, *J. Phys. Chem.* **1991**, *95*, 3289.
- [7] a) T. J. Marks, *Acc. Chem. Res.* **1992**, *25*, 57; b) C. Copéret, M. Chabanas, R. Petroff Saint-Arroman, J.-M. Basset, *Angew. Chem. Int. Ed.* **2003**, *42*, 156; c) C. Copéret, A. Comas-Vives, M. P. Conley, D. P. Estes, A. Fedorov, V. Mougél, H. Nagae, F. Núñez-Zarur, P. A. Zhizhko, *Chem. Rev.* **2016**, *116*, 323.
- [8] a) K. L. Furdala, T. D. Tilley, *Chem. Mater.* **2001**, *13*, 1817; b) C. Nozaki, C. G. Lugmair, A. T. Bell, T. D. Tilley, *J. Am. Chem. Soc.* **2002**, *124*, 13194; c) R. L. Brutchey, I. J. Drake, A. T. Bell, T. D. Tilley, *Chem. Commun.* **2005**, 3736; d) K. Furdala, R. Brutchey, T. D. Tilley, in 'Surface and Interfacial Organometallic Chemistry and Catalysis', Eds. C. Copéret, B. Chaudret, Springer Berlin Heidelberg, **2005**, Vol. 16, p 69.
- [9] V. Mougél, K.-W. Chan, G. Siddiqi, K. Kawakita, H. Nagae, H. Tsurugi, K. Mashima, O. Safonova, C. Copéret, *ACS Cent. Sci.* **2016**, *2*, 569.
- [10] D. P. Estes, G. Siddiqi, F. Allouche, K. V. Kovtunov, O. V. Safonova, A. L. Trigub, I. V. Koptuyg, C. Copéret, *J. Am. Chem. Soc.* **2016**, *138*, 14987.
- [11] A. M. Bryan, G. J. Long, F. Grandjean, P. P. Power, *Inorg. Chem.* **2013**, *52*, 12152.
- [12] R. S. Drago, 'Physical Methods for Chemists', 2nd ed., Saunders College Publishing: New York, NY, **1977**.
- [13] a) H. Funke, M. Chukalina, A. C. Scheinost, *J. Synchrotron Radiat.* **2007**, *14*, 426; b) J. Timoshenko, A. Kuzmin, *Comput. Phys. Commun.* **2009**, *180*, 920; c) T. J. Penfold, I. Tavernelli, C. J. Milne, M. Reinhard, A. E. Nahhas, R. Abela, U. Rothlisberger, M. Chergui, *J. Chem. Phys.* **2013**, *138*, 014104.
- [14] a) J. M. Mayer, *Acc. Chem. Res.* **1998**, *31*, 441; b) N. Dietl, M. Schlangen, H. Schwarz, *Angew. Chem. Int. Ed.* **2012**, *51*, 5544.
- [15] a) F. D. Kopinke, G. Zimmermann, K. Anders, *J. Org. Chem.* **1989**, *54*, 3571; b) S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **2003**, *36*, 255. Marcus theory suggests that at 823 K the tertiary C–H bond in isobutane (96.5 kcal/mol) should react about twice as fast as the secondary one in propane (98.6 kcal/mol) (ignoring differences in the self exchange rate constants). This matches observed H<sup>+</sup> transfer rates quite well, as shown in ref. [15a]. However, since propane has two secondary C–H bonds versus the one tertiary C–H bond in isobutane, propane and isobutane would be expected to have the same TOF.
- [16] J. Hartwig, 'Organotransition Metal Chemistry', University Science Books, Sausalito, CA, **2010**.
- [17] a) A. Zecchina, C. O. Arean, *Chem. Soc. Rev.* **1996**, *25*, 187; b) A. J. Lupinetti, S. H. Strauss, G. Frenking, in 'Progress in Inorganic Chemistry', John Wiley & Sons, Inc., **2001**, p 1.
- [18] a) O. G. Salnikov, K. V. Kovtunov, D. A. Barskiy, V. I. Bukhtiyarov, R. Kaptein, I. V. Koptuyg, *App. Mag. Res.* **2012**, *44*, 279; b) K. V. Kovtunov, V. V. Zhivonitko, I. V. Skovpin, D. A. Barskiy, I. V. Koptuyg, in 'Hyperpolarization Methods in NMR Spectroscopy', Ed. T. L. Kuhn, Springer Berlin Heidelberg, **2013**, p 123; c) V. P. Ananikov, L. L. Khemchyan, Y. V. Ivanova, V. I. Bukhtiyarov, A. M. Sorokin, I. P. Prosvirina, S. Z. Vatsadze, A. V. Medved'ko, V. N. Nuriev, A. D. Dilman, V. V. Levin, I. V. Koptuyg, K. V. Kovtunov, V. V. Zhivonitko, V. A. Likhobolov, A. V. Romanenko, P. A. Simonov, V. G. Nenajdenko, O. I. Shmatova, V. M. Muzalevskiy, M. S. Nechaev, A. F. Asachenko, O. S. Morozov, P. B. Dzhevakov, S. N. Osipov, D. V. Vorobyeva, M. A. Tpchij, M. A. Zotova, S. A. Ponomarenko, O. V. Borschchev, Y. N. Luponosov, A. A. Rempel, A. A. Valeeva, A. Y. Stakheev, O. V. Turova, I. S. Mashkovskiy, S. V. Sysolyatin, V. V. Malykhin, G. A. Bukhtiyrova, A. O. Terent'ev, I. B. Krylov, *Russ. Chem. Rev.* **2014**, *83*, 885.
- [19] a) D. Balcells, E. Clot, O. Eisenstein, *Chem. Rev.* **2010**, *110*, 749; b) J. R. Webb, S. A. Burgess, T. R. Cundari, T. B. Gunnoe, *Dalton Trans.* **2013**, *42*, 16646.
- [20] R. Wischert, P. Laurent, C. Copéret, F. Delbecq, P. Sautet, *J. Am. Chem. Soc.* **2012**, *134*, 14430.