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C–H Activation

On the Mechanism of the Palladium Bis(NHC) Complex Catalyzed CH Functionalization of Propane: Experiment and DFT Calculations**

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Abstract: We report a detailed mechanistic study on the CH functionalization of alkanes by palladium complexes with chelating bis(*N*-heterocyclic carbene) (NHC) complexes. The experimental results are complemented by detailed DFT calculations, which allow us to rationalize the regioselectivity and the catalytic activity. The study includes a library of catalysts with different electronic and steric properties, kinetic data, and isotope effects. The combined experimental and computational results favor a mechanism involving organometallic palladium(IV) intermediates. Furthermore, it is shown that at high halide loadings a different mechanism is operative.

Introduction

The functionalization of hydrocarbons has been one of the most exciting areas of catalysis for decades. Likewise, the refinement of natural gas is becoming increasingly important because of the enormous shale gas boom in North America.[1] It has been predicted that, unlike coal and crude oil, the share of natural gas in global energy consumption is going to increase considerably during the next 25 years.[2]

Unfortunately, the gaseous state of natural gas renders its transport challenging and billions of cubic meters of natural gas are flared or vented annually. The CO-involving Fischer–Tropsch process, which is commercially used by Sasol and Shell, is very energy demanding as well. Therefore, the development of an efficient chemical process, which ideally converts methane directly to methanol, is highly desirable. Direct and selective oxidative strategies do not suffer from those drawbacks. Homogeneous transition-metal-mediated CH functionalization protocols appeared to be promising and have been studied in detail by numerous research groups.[3]

However, even 45 years after the seminal work of Shilov,[4] the development of an efficient methane CH-functionalization process using a reasonable reaction medium and cheap oxidant remains elusive. The most prominent example constitutes the platinum-based Catalytica system, which uses oleum as solvent and oxidant.[5] Similarly, the aerobic functionalization of methane with manganese and cobalt salts in trifluoroacetic acid (HOTFA) suffers from catalyst deactivation phenomena.[6] Radical pathways, which are compatible with aqueous reaction environments, usually suffer from low chemoselectivity and/or the usage of unfavorable oxidants.[7]

Palladium compounds were also studied in the context of alkane functionalization[8] and were even considered for industrial application.[9] We have shown that palladium catalysts, which are stabilized by chelating bis-*N*-heterocyclic carbene (NHC) ligands, exhibit very high catalytic activity with methane in trifluoroacetic acid at 90 °C, using $K_2S_2O_8$ as oxidant.[10] Later, we evaluated the reactivity of a series of palladium bis(NHC) catalysts with propane.[11]

We also modeled the mechanism of the palladium-bis(NHC) complex catalyzed CH functionalization of methane by means of DFT calculations.[12] We proposed, based on previous work and the synthesis and reactivity of potential intermediates (Figure 1),[13] that the reaction proceeds with a palladium catalyst in the oxidation states of +II and +IV.

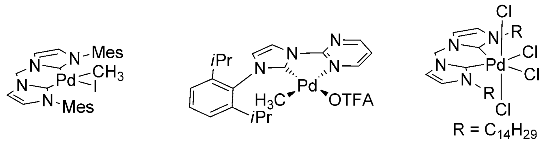

Figure 1. Synthesized potential intermediates.

The CH activation step probably takes place with a palladium(II) complex (Scheme 1) and is followed by a bromine-mediated oxidation to produce a palladium(IV) alkyl species. The trifluoroacetate ester is then released by reductive elimination through external nucleophilic attack by a trifluoroacetate molecule. The intermediately active oxidant bromine can be regenerated by oxidants like $K_2S_2O_8$, which thereby produce the catalytically potent complex **1** by an oxidative exchange of the bromido for trifluoroacetato ligands.

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[**] *NHC = N-heterocyclic carbene.*

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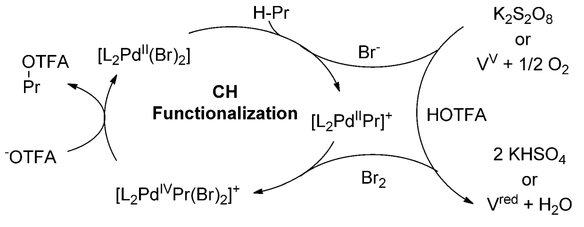


Scheme 1. Proposed mechanism for the aerobic partial oxidation of propane. V^V: $NaVO_3$. V^{red}: vanadium-oxo compound with an oxidation state lower than +V.

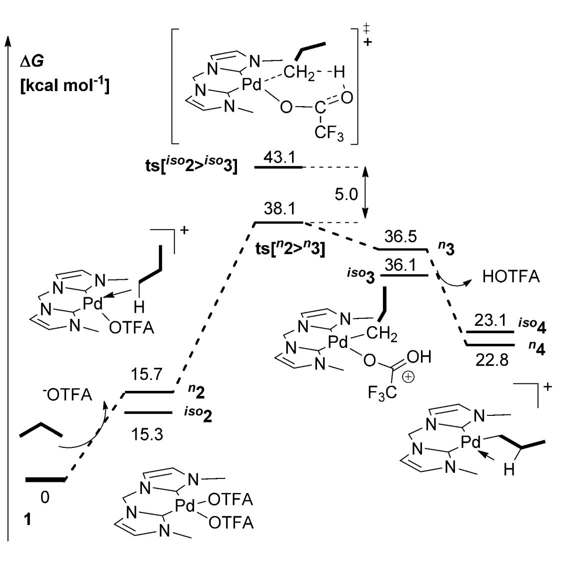
Very recently, we discovered that the reaction with propane can be run with molecular oxygen as terminal oxidant in the presence of a $NaVO_3$ co-catalyst and bromide.[14] Our results therefore constitute an example of aerobic generation of palladium in the oxidation state of +IV.[15,16] DFT calculations[17] suggested that a mixture of neutral and charged species are present under the reaction conditions prior to the formation of the catalytically competent species **1**.

Herein, we report detailed mechanistic investigations, including DFT calculations[18] on the CH functionalization of propane by palladium bis(NHC) catalysts. We will rationalize why the reaction proceeds with *iso*-selectivity and report the selectivity and rate determining step of the reaction. Calculated reaction barriers will be shown to correlate with the catalytic activity of a series of bis(NHC) complexes.[11] We will comment on the kinetics of the reaction and on the stoichiometric reactivity of potential intermediates of the catalytic cycle.

Results and Discussion

CH Activation

The CH activation (Scheme 2) is predicted to take place after the endergonic formation of the cationic, propane-coordinating palladium σ complexes **^{n}2** (15.7 kcal mol^{-1}) or **^{iso}2** (15.3 kcal mol^{-1}). The subsequent CH bond activation (**ts[^{n}2 > ^{n}3]** and **ts[^{iso}2 > ^{iso}3]**) is calculated to proceed by a cationic, intramolecular transition state, preferentially at one of the terminal methyl groups of propane ($\Delta\Delta G^{\neq} = 5.0$ kcal mol^{-1}). Opposed to the kinetic selectivity, the *iso*-product **^{iso}3** is thermodynamically more stable than the *n*-product **^{n}3** by 0.4 kcal mol^{-1}. The palladium *n*-alkyl product **^{n}3** and *iso*-alkyl isomer **^{n}3** are considerably stabilized (22.8 kcal mol^{-1} and 23.1 kcal mol^{-1}) by the dissociation of the weakly coordinating HOTFA molecule and the formation of a β agostic interaction in the intermediates **^{n}4** or **^{iso}4**.

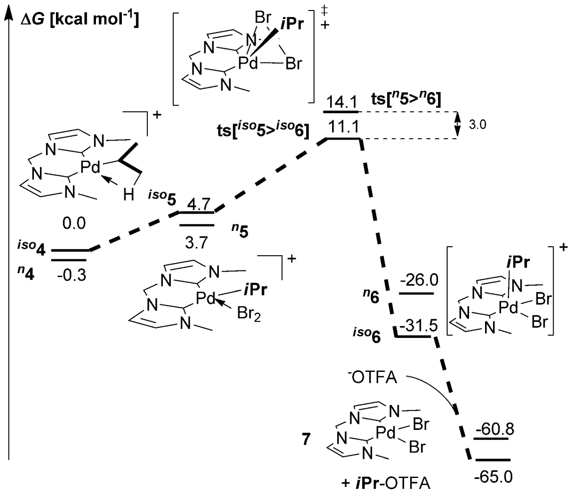


Scheme 2. CH Activation at the *iso*- and *n*-position of propane. Values are given in kcal mol^{-1}. V^v and V^{red} are defined as in Scheme 1.

Oxidation and product formation

Bromine can replace the agostic interaction in **^{n}4** and **^{iso}4** by coordinating to the palladium atom in compounds **^{n}5** and **^{iso}5**. The oxidative addition of bromine to produce **^{n}6** or **^{iso}6** (Scheme 3, Figure 2) then proceeds via the transition states **ts[^{n}5>^{n}6]** (14.1 kcal mol^{-1}) or **ts[^{iso}5>^{iso}6]** (11.1 kcal mol^{-1}).

The kinetic preference for oxidation of the *iso*-intermediate **^{iso}5** is also reflected by the greater thermodynamic stability of the palladium(IV) product **^{iso}6** (−31.5 kcal mol^{-1}) versus **^{n}6** (−26.0 kcal mol^{-1}). Compounds **^{iso}6** and **^{n}6** can then easily reductively eliminate the corresponding *n*- or *iso*- trifluoroacetic acid ester.



Scheme 3. Oxidation and reductive elimination. Values are given in kcal mol^{-1}.

Figure 2 illustrates that the bond length of the forming Pd–Br bond in the *iso* transition state **ts[^{iso}5 > ^{iso}6]** is longer by 0.06 Å compared to the *n* transition state **ts[^{n}5 > ^{n}6]**. The preference for the *iso*-transition state is mainly due to electronic reasons. The oxidation of the palladium(II) complex to the corresponding palladium(IV) compound entails an increasing positive partial charge on the palladium atom (natural populations analysis (NPA)[19] charges, values given in atomic units: **^{iso}5**: +0.43 a.u.; **^{iso}6**: +0.59 a.u.; **^{n}5**: +0.43 a.u.; **^{n}6** +0.66 a.u.). As the

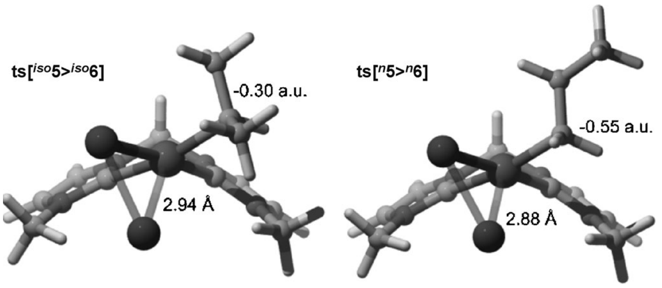


Figure 2. Oxidative addition transition states **ts[^{iso}5>^{iso}6]** and **ts[^{n}5>^{iso}6]**. Bond lengths are given in [Å], NPA charges in a.u.

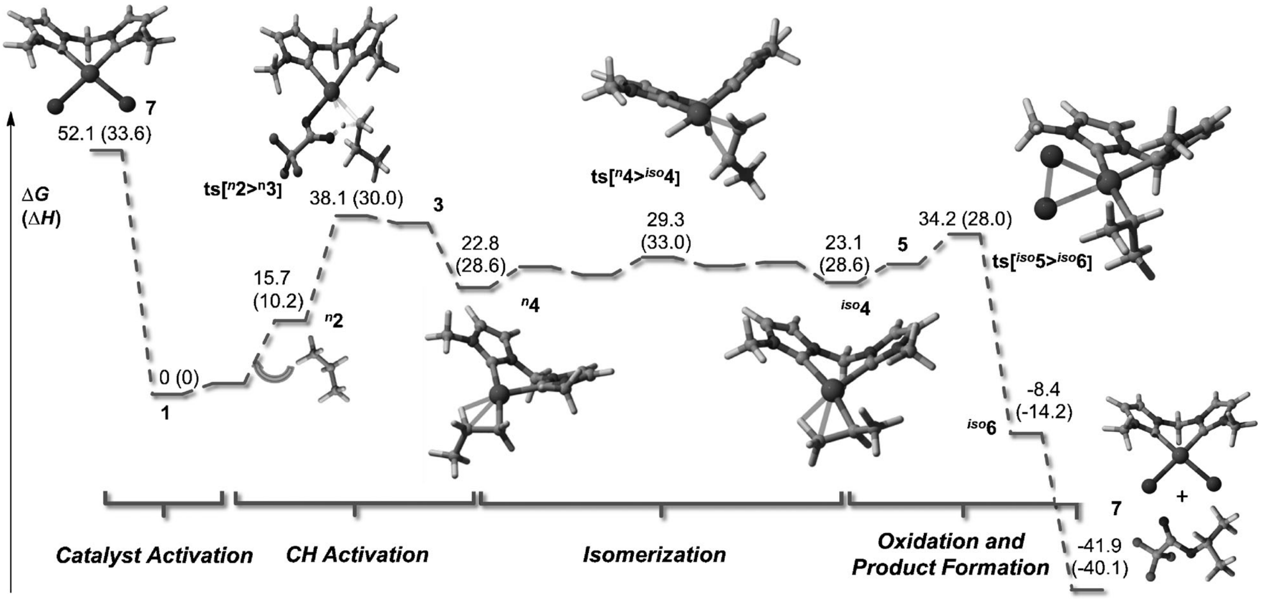
iso-propyl substituent is a stronger electron donor than the *n*-propyl substituent, the corresponding transition state **ts[^{iso}5 > ^{iso}6]** shows an enhanced stabilizing charge transfer from the bonding carbon atom to the transition metal (NPA charges: **ts[^{iso}5 > ^{iso}6]**: −0.30 a.u.; **ts[^{n}5 > ^{n}6]**: −0.55 a.u.). Most interestingly, this umpolung process[20] facilitates the nucleophilic attack by trifluoroacetate leading finally to the liberation of *iso*-propyl trifluoroacetate.

Isomerization

Compound **^{n}4** can interconvert to **^{iso}4** via an isomerization/migratory insertion reaction sequence (Supporting Information, Figure S1). β-Hydride elimination in intermediate **^{n}4** leads to the formation of a propene-coordinating π-complex **4_π**. Rotation around the propene double bond (**ts[^{n}4 > ^{iso}4]**) and migratory insertion of the hydride atom produces compound **^{iso}4**. This reaction sequence proceeds with a relatively low reaction barrier ($\Delta G^{\neq} < 5$ kcal mol^{-1}). We conclude that the different *n*- and *iso*-alkyl compounds can potentially exist in equilibrium with each other. Even chelating bis(NHC) ligands with bulky tert-butyl groups seem to be incapable of preventing this isomerization process efficiently. This is in line with our experimental observation of the predominant formation of the *iso*-product (see below in Figure 7 and Supporting Information Figures S2–S4). Consequently, reaction mechanisms involving the reductive elimination from palladium in the oxidation state +IV are predicted to preferentially yield the *iso*-functionalized product.

Discussion of the DFT calculated mechanism

Scheme 4 shows the ΔG (and ΔH) values for the most favorable calculated mechanism. The catalytic cycle starts with the preactivation of **7** by oxidative substitution of the strongly coordinating bromido for weakly coordinating trifluoroacetato ligands (**1**, $\Delta G = -52.1$ kcal mol^{-1}). The CH activation step takes place at one of the CH_3 groups of propane and produces the *n*-alkyl palladium species **^{n}4**. This alkyl palladium species isomerizes to the corresponding *iso*-propyl compound **^{iso}4**. The oxidation of compound **^{iso}4** to palladium(IV) is mediated by bromine and followed by the reductive elimination of the *iso*-propyl ester. The oxidation reaction proceeds with an overall reaction barrier of 34.2 kcal mol^{-1}, whereas the CH activation step is predicted to have a reaction barrier of 38.1 kcal mol^{-1}. Therefore, the regioselectivity of the overall reaction (where oxidation is the selectivity-determining step) is not established within the rate-determining step (CH activation). The calculated rate-determining transition state predicts a kinetic isotope effect (KIE) between perprotio and perdeuterio propane of 4.1 at 60 °C. A comparison of the ΔG and ΔH values reveals that the reaction proceeds with a negative entropy ($\Delta S < 0$). Nevertheless, considering the uncertainties related to the calculation of ΔS values of processes associated with ligand dissociation and charge separation, we do not want to put too much weight on the calculated absolute values.[21] Electrophilic mechanisms without the intermediate formation of carbon–



Scheme 4. Most favorable calculated mechanism. ΔG (ΔH) values are given in kcal mol^{-1}.

transition metal bonds have been investigated as well, but were predicted to have prohibitively high reaction barriers ($\Delta G^{\neq} > 52\ \mathrm{kcal\,mol^{-1}}$, Figure S2 in the Supporting Information).

The combined results are in line with the literature, as the *n*-selectivity, which is often observed in case of transition-metal-mediated CH activation chemistry, has been reported to be very small or even reversed in the case of (especially cationic) palladium(II) catalysis.[22] Very detailed DFT calculations reported by Harvey rationalized the preferential formation of the *iso* branched product for chelating palladium diimine complexes with electronic reasons.[23] Notably, Harvey also described an enhanced selectivity for the *iso*-product in case of cationic palladium complexes.

In order to experimentally evaluate the plausibility of our calculated rate-determining step, we determined the Arrhenius parameters and the isotope effect of the reaction.[14a] The Arrhenius energy of activation was determined to be (29.0 ± 1.6) kcal mol^{-1}, which fits nicely to the calculated ΔH value of 30.0 kcal mol^{-1}. Also the isotope effect of 3.4 ± 0.8, which was obtained for the model substrate cyclohexane, is in good agreement with calculated values (cyclohexane = 3.9, propane = 4.1). Both experimental values confirm that the CH-activation step is the rate determining state of the reaction. We also observed that the addition of water and even of trifluoroacetic anhydride led to an inhibition of the reaction. This can also be rationalized by our calculations,[12] as the rate-determining transition state is cationic in nature.[24] The DFT-calculated mechanism has a number of further implications, which could be verified by experimental investigations. The reaction is expected to proceed without an induction period and with a 1st order rate law regarding the catalyst's concentration. A zero order rate law is expected for a soluble[25] oxidant, as it is not directly involved in the rate-determining step (CH activation). Furthermore, the activity of catalysts with different bis-(NHC) ligands should be correlated to the calculated barriers for the rate determining state.

Rate laws

The kinetics of the reaction was studied. We did not observe a significant induction period or signs of decomposition of the palladium catalyst after a reaction time of 23 h. A plot of the reaction kinetics (Figure 3) confirms that the reaction is not dependent on the concentration of oxidant (approximately zero order) for the first 12 h (≈50 % yield based on oxidant) at an oxidant loading of 400 equiv to the catalyst. We therefore conclude that the oxidant is not involved in the rate-determining step. The reaction furthermore exhibits a dependence on a 1st order reaction rate relative to the catalyst's and substrate's concentrations, as predicted by the calculations.[14a] In conclusion, all the obtained kinetic data and rate laws agree with the proposed mechanism.

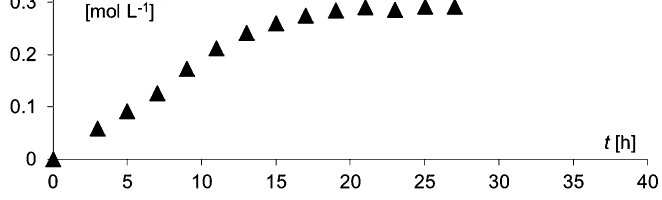


Figure 3. Kinetic profile. Reaction conditions: 113 μmol **7**, 400 equiv $K_2S_2O_8$, 67.5 mL HOTFA, 60 °C, 6 bar propane.

Formation of CO_2

We detected the formation of carbon dioxide during the course of the reaction, which can be attributed to the decarboxylation of trifluoroacetic acid. The amount of CO_2 formed accounts roughly for the observed low mass balance in $K_2S_2O_8$. We also determined a loss of about 1–2 mL of solvent in the kinetic experiment shown in Figure 3. Hence, our results indicate that radical oxidation of the solvent by $K_2S_2O_8$ to CO_2 occurs. This pathway, which has been proposed to lead to CH activation by the generation of CF_3 radicals[26] is definitely not involved in the case of the oxidants Selectfluor or $NaVO_3/O_2$, where we did not detect the formation of CO_2.[14a] Also, this pathway does not contribute considerably to the formation of the trifluoroacetate ester under our reaction conditions with $K_2S_2O_8$, as no effect of adding radical transfer/trapping reagents to the reaction was observed.[14]

Alkylbromides

The DFT-calculated mechanism involves the reductive elimination of *iso*-propyl trifluoroacetate from a palladium(IV) intermediate with bromido ligands. Our calculations for methane had predicted that the reductive elimination by reaction with trifluoroacetate is favored over reductive elimination of the corresponding bromoalkyl compound.[12] Nevertheless, we wanted to verify if alkylbromides are indeed not viable intermediates of the catalytic cycle. Therefore, 2-bromopropane was subjected to the reaction conditions (Figure 4). However, as it did not react, there is no reason to believe that it is an intermediate of the catalytic cycle.

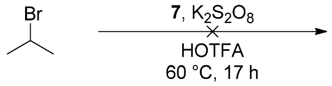


Figure 4. 2-Bromopropane is not a viable intermediate of the catalytic cycle. Reaction conditions: 1.3 μmol **7**, 2.7 μmol $K_2S_2O_8$, 50 μL 2-bromopropane, 0.8 mL HOTFA, 60 °C, 17 h.

Next, we turned our attention towards the effect of adding bromide salts to the reaction. As already reported,[14] the addition of two or five equivalents of KBr to the reaction mixture led to an almost quantitative inhibition of the reaction with very little (supposedly radical) background reactivity (4.2 μmol **7**, 8.4 μmol or 21 μmol KBr, 210 μmol $K_2S_2O_8$, 1 bar propane, 2.5 mL HOTFA, 60 °C, 17 h: TON = 4 and TON = 2, compared to TON = 18 without addition of KBr). Surprisingly, we also observed the formation of *iso*-propyl bromide and *iso*-propyl tri-

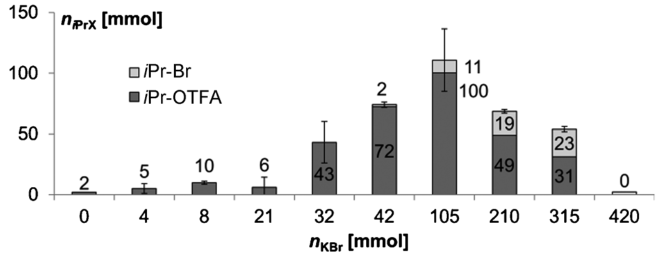


Figure 5. Autocatalysis at high loadings of KBr. 210 μmol $K_2S_2O_8$, 2.5 mL HOTFA, 1 bar propane, 60 °C, 17 h.

fluoroacetate, if we further increased the amount of KBr to eight equivalents (32 μmol, TON = 11). Further investigations revealed that the reactivity is not associated with the palladium catalyst (Figure 5).

The reaction proceeds with extraordinary chemo- and regioselectivity. We did not detect the formation of *n*-alkyl, difunctionalized, or any other products, but the formation of moderate amounts of 2-bromopropane at KBr loadings of 42 μmol or higher. This points towards a different reaction mechanism than for the palladium catalysts. Remarkably, the maximum yield was obtained at a $KBr/K_2S_2O_8$ ratio of 0.5:1. The virtually quantitative *iso*-selectivity could be explained by a mechanism involving electrophilic, positively charged bromo species. Related I^+ reactivity was proposed for the oxidation of methane in oleum[27] and was also discussed for LiBr in the presence of periodates.[3f,28] Very recent work demonstrated that the presence of chloride salts is decisive for the very efficient and selective oxidation of methane to methyl trifluoroacetate.[29] We conclude that this area of hydrocarbon functionalization looks very promising, but does not appear to be the preferential pathway in the presence of low concentrations of **7** or for palladium acetate.

Stoichiometric reactivity

The stoichiometric reactivity of the palladium(II) complexes **7** and **1** with propane and cyclohexane was evaluated. The DFT calculations predict **7** and **1** to be catalytically inactive, as the CH functionalization is proposed to be mediated by a cationic palladium(II) complex. The resulting intermediate needs to be oxidized subsequently by an oxidant. Indeed, we did not observe the formation of alkyl trifluoroacetates or alkyl halides, and the complexes appeared to be perfectly stable in refluxing trifluoroacetic acid in the presence of propane. Also, the in situ exchange of the bromido ligands by two equivalents of AgOTf did not result in the formation of trifluoroacetoxylated products. We conclude that, contrarily to the reactivity of $Pd(OAc)_2$,[8c] activation by palladium(II), followed by reductive elimination to palladium(0), is not a viable reaction mechanism.

In order to prove the formation of palladium(IV) species in the reaction mixture, we added $K_2S_2O_8$ to a solution of **7** in HOTFA (14 h, 60 °C). We thereby observed a reddish precipitate, which we attribute to the formation of unstable and insoluble palladium(IV) complexes $\mathbf{L_2Pd^{IV}(X)_4}$ (L_2 = bis(NHC) ligand) as described by Kraft.[13d] A ^{1}H NMR spectrum revealed the existence of at least two different bis(NHC) complexes in solution (Figure 6). Apart from the starting material, it showed signals at 4.17 (CH_3), 6.98 (CH_2), 7.15 (CH_2), 7.56 (CH_2) and a broad signal at 8.01 ppm (CH). When adding bromine to a solution of **7** in trifluoroacetic acid, we observed the formation of a very similar signal set, which can be assigned to a palladium species in the oxidation state +IV.[13b,d] Accordingly, the addition of not only bromine, but also of $K_2S_2O_8$, to **7** in trifluoroacetic acid, leads to the formation of a mixture of palladium(II) and palladium(IV) compounds. This mixture constitutes the resting state of the catalyst.

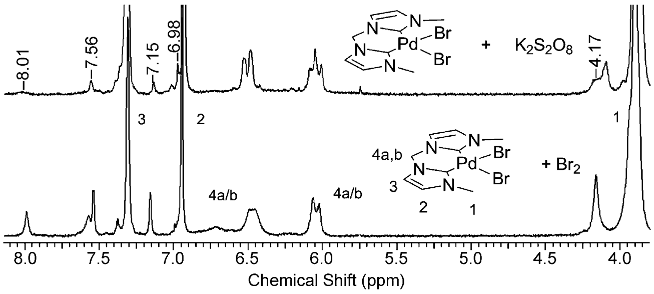


Figure 6. Formation of $\mathbf{L_2Pd^{IV}(X)_4}$ after addition of oxidant as evidenced by ^{1}H NMR spectroscopy. Upper spectrum: Signals of **7** after addition of $K_2S_2O_8$ in HOTFA. Lower spectrum: Signals of **7** after addition of Br_2 in HOTFA with assignments of signals for **7**.

Finally, the catalytic activity of the palladium(IV) complex $\mathbf{L_2Pd^{IV}(X)_4}$ was investigated. However, no significant reactivity was obtained even after the addition of silver triflate. In agreement with the DFT calculations, CH activation by palladium(IV) species does not appear to be part of the operating reaction mechanism.

Structure–activity relationship

After having established the nature of the rate determining step, we evaluated whether or not we could rationalize the catalytic activity of palladium catalysts with different bis(NHC) ligands. Indeed, the calculations turned out to predict the experimental results fairly well. Figure 7 shows the correlation between the calculated overall Gibbs free energy of activation and the catalytic turnover (TON) after 12 h for an extended[11] series of palladium bis(NHC) catalysts. Less-electron-rich benzimidazolylidene catalysts are predicted to show considerably lower activity than their imidazolylidene counterparts, which is in agreement with our experimental data. The same applies for the *ortho*-phenylene bridged catalysts with bromo substituents at the phenyl ring compared with substitution with hydrogen substituents. Very impressively, even the small steric effects of the *tert*-butyl, methyl, or benzyl ligand wingtips are rationalized by the calculations. Therefore, the calculations could serve as a predictive tool for the further development of more active and selective catalysts, as long as the rate-determining state does not change.

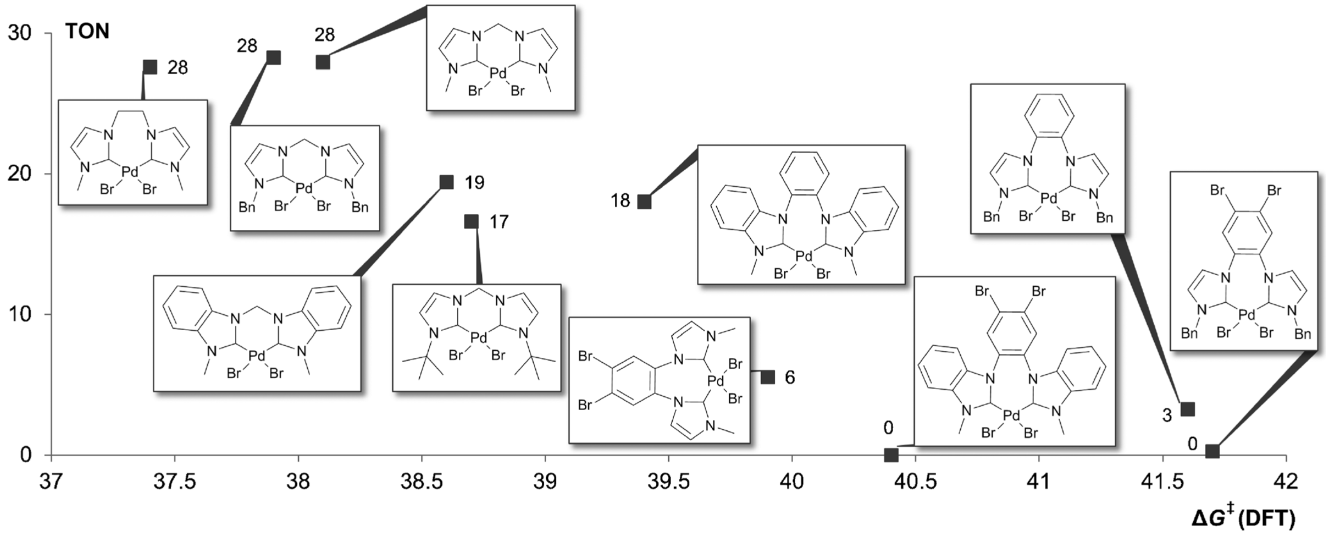


Figure 7. Correlation between the observed catalytic activity (TON) and the reaction barrier ($\Delta G^{\neq}$) as predicted by DFT (i.e., **1** and **ts[^{n}2>^{n}3]**). Reaction conditions: 8.4 μmol catalyst, 0.84 mmol $K_2S_2O_8$, 5.0 mL HOTFA, 60 °C, 12 h. Values are given in kcal mol^{-1}.

Conclusion

The mechanism of the bis(NHC) palladium complex catalyzed functionalization of propane was studied in detail. We report and discuss DFT calculations, kinetic data, stoichiometric reactivity, rate laws, solvent effects, ligand–catalytic activity relationship, and the activation energy. The experimental results are in agreement with the predictions by DFT. There is a strong indication that the CH-activation step takes place at a palladium(II) complex and is followed by an oxidation by bromine to the oxidation state +IV. The combined results of DFT calculations and experiments are indicative that the CH-activation step controls the reaction rate, whereas the *iso*-selectivity is being determined within the oxidation step to palladium(IV). A different mechanism with remarkably high chemoselectivity was shown to be operative at high loadings of bromine salts. We believe that our DFT calculations will guide further improvements regarding the ligand design and will support the development of novel aerobic cooxidation procedures.

Experimental Section

DFT Calculations

The calculation have been performed with Gaussian03 at the SP//B3LYP/6–31G(d) level of theory using a Hay–Wadt effective core potential (SP: B3LYP-D3[SCRF(CPCM)]/6–311++G(d,p)) and according to our previous reports.[12,17,30] Further details and the full Gaussian citation are given in the Supporting Information.

Experimental details

Caution: Many of the reagents and reaction conditions are potentially hazardous.

Proper safety precautions should be implemented!

All palladium bis(NHC) complexes were synthesized as reported in the literature.[10c,11,31] All chemicals were obtained by commercial suppliers and used without further purification. KBr with a purity of 99.999 % has been used.

The catalyses described in Figure 7 were conducted as previously reported[11] and were run in 10 mL crimp-top vials with PTFE-faced butyl rubber septa. Palladium (8.4 μmol) catalyst and $K_2S_2O_8$ (0.84 mmol) were suspended in HOTFA (5 mL). In cases where the catalyst amount was less than 5 mg, stock solutions of the catalyst in HOTFA were freshly prepared. Subsequently, propane was bubbled through the suspension for 60 seconds. The vials were sealed immediately and it was stirred vigorously at 60 °C for 12 h. The reaction mixture was analyzed by gas chromatography with an Agilent 6850 Series II Networked GC equipped with a flame ionisation detector (FID) and a Macherey–Nagel Optima-210 0.25 μm column (30 m × 0.25 mm). Quantification of the yield of the reaction products was done by adding C_6F_5Cl (25 μL) as standard to the reaction mixture (1.00 mL) and injection of this mixture into the GC. Reported TONs are based on *iso*-propyl trifluoroacetate only. The identity of the reaction products was confirmed by comparison with the retention time of defined samples and ^{1}H NMR spectra of the reaction mixtures in an NMR tube, which contained a capillary filled with [D$_6$]DMSO to provide a lock signal. All GC measurements were repeated four times and catalyses twice. Given values are averaged over all measurements. For the examination of the reactivity of *iso*-propyl bromide, 1.3 μmol **7**, 2.7 μmol $K_2S_2O_8$ and 50 μL 2-bromopropane were added to 0.8 mL HOTFA in the 10 mL crimp top vial, which was sealed subsequently. The reaction mixture was analyzed by GC-FID after stirring for 17 h at 60 °C.

For the determination of the kinetics (Figure 3), 113 μmol of **7** and 45.2 mmol $K_2S_2O_8$ were added to 67.5 mL of HOTFA in a 160 mL Hastelloy C-2000 reactor by *Parr*. The reactor was purged three times with 7 bar of propane and then filled with 7 bar of propane. It was stirred at 500 rpm and 60 °C. Samples were taken in situ with the help of a sampling valve and analyzed by GC-FID at the indicated time points.

The analysis of the gas headspace was performed with an Agilent 6850 Series II Networked GC, equipped with a thermal conductivity detector (TCD) and a J&W Scientific GS-GasPro column (60 m ×

0.32 mm). Gas samples were taken from the reactor at room temperature with a custom build 1.5 mL high pressure gas mouse after the reaction. The gas sample was then expanded into an open-ended 1 mL sample loop at the GC. Identification and quantification of the detected gases was accomplished by comparing retention times and signal areas with measurements of standard gas mixtures with known gas compositions.

For the stoichiometric oxidation of **7**, the catalyst (31 μmol) was dissolved in a screw cap NMR tube in trifluoroacetic acid (0.36 mL). Trifluoroacetic acid (0.04 mL) was added in order to guarantee water-free conditions. The NMR tube contained a capillary filled with [D$_6$]DMSO in order to provide a lock signal. The NMR tube was sealed quickly after suspending $K_2S_2O_8$ (31 μmol) and heated overnight at 60 °C, where it was kept under constant vibration. The spectra were recorded on a Bruker AC 300P spectrometer.

The experiment with **$L_2Pd^{IV}(Cl)_4$** was conducted accordingly, but AgOTf was added instead of $K_2S_2O_8$ and propane was bubbled through the reaction mixture for 30 seconds prior to sealing the screw cap NMR tube. The reactivity of **7** and **1** with propane was studied likewise. For cyclohexane, 28 μL (256 μmol) were added to the reaction mixture instead of saturating it with propane.

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