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Alkane C−H Functionalization and Oxidation with Molecular Oxygen

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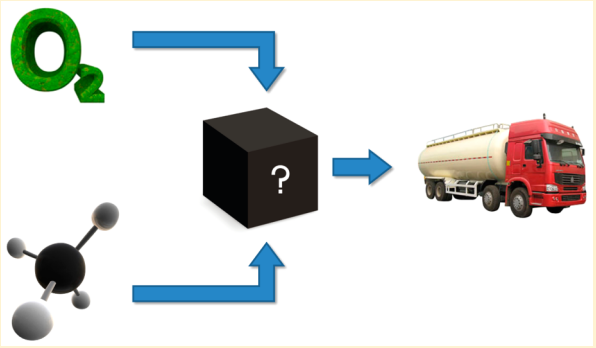
ABSTRACT: The application of environmentally benign, cheap, and economically viable oxidation procedures is a key challenge of homogeneous, oxidative alkane functionalization. The typically harsh reaction conditions and the propensity of dioxygen for radical reactivity call for extraordinary robust catalysts. Mainly three strategies have been applied. These are (1) the combination of a catalyst responsible for C−H activation with a cocatalyst responsible for dioxygen activation, (2) transition-metal catalysts, which react with both hydrocarbons and molecular oxygen, and (3) the introduction of very robust main-group element catalysts for C−H functionalization chemistry. Herein, these three approaches will be assessed and exemplified by the reactivity of chelated palladium (N-heterocyclic carbene) catalysts in combination with a vanadium cocatalyst, the methane functionalization by cobalt catalysts, and the reaction of group XVII compounds with alkanes.



INTRODUCTION

Annually, more than 140 billion cubic meters of natural gas are flared worldwide for safety reasons.[1] Imagine if valuable methanol or other oxygenated, liquid products were formed instead of CO_2, which constitutes a primary greenhouse gas. Would that not be great?[2−4] Since the seminal findings by Shilov,[5−7] who showed that the late transition metals platinum and palladium are capable of oxidizing lower hydrocarbons selectively to alcohols, it has been shown that most elements of the periodic table can react with C−H bonds. This includes early transition metals[8−13] and arguably, most prominently, late transition metals[14−31] like cobalt, rhodium, iridium, palladium, and platinum as well as main-group metals like thallium or lead.[32] Some examples of defined transition-metal complexes that activate C−H bonds of lower alkanes are given in Figure 1. Obviously, also nonmetallic C−H bond activation has been known since the very beginning of organic chemistry, including the radical and nonradical reactivity of halogens with alkanes[33−35] and the reactivity of low-valent compounds like carbenes,[36,37] borylenes,[38] or aluminum compounds.[39] Even in nature, C−H activation of alkanes is by no means rare, as exemplified by cytochrome P450[40−44] or methane monooxygenase.[45−49] Consequently, the development of a catalytic process, in a homogeneous or heterogeneous context like a fuel cell,[50−53] for C−H activation and functionalization of a hydrocarbon with a convenient oxidation protocol involving molecular oxygen appears to be a very attractive goal.[54−57]

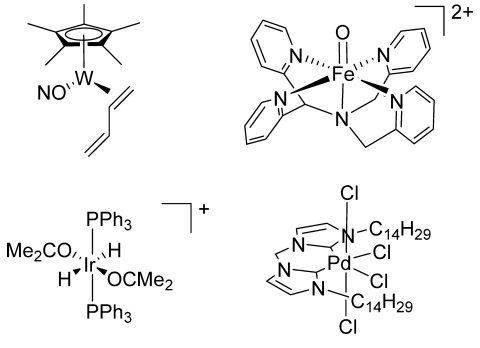


Figure 1. Transition-metal complexes that react with the C−H bonds of lower alkanes.[13,62−64]

Although the activation of C−H bonds (leading, e.g., to an organometallic intermediate) does not necessarily involve species in high oxidation states,[58] the oxidative C−H oxyfunctionalization of methane typically requires strong oxidants, as also illustrated by the comparably high ionization energy of 12.7 eV.[7,59] However, because of the difficulties in developing a system that is based on dioxygen (O_2), several other oxidants have been used. These certainly are not the solution for a commercial process, where O_2 needs to be the coreactant, but allow one to study the conversion of alkanes.[60,61] Frequently critical are also the stability and reactivity of homogeneous C−H functionalization catalysts.

Herein, fundamental approaches to aerobic hydrocarbon functionalization will be discussed on the basis of three concepts exemplifying our approach toward the functionalization of methane and propane and put into context to closely related work.

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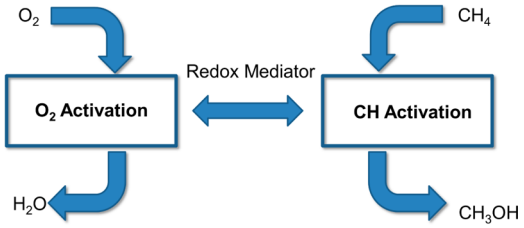
ALKANE ACTIVATION USING REDOX MEDIATORS

Three different oxidation concepts, by a chemical point of view, can be envisioned for the aerobic functionalization of lower hydrocarbons. In the first scenario, the catalytic cycles for C−H and O_2 activation are separated and could therefore, in principle, be spatially distinct in a tandem catalysis arrangement (Scheme 1). ***Safety Note!*** *It is important to note that mixtures of hydrocarbons with strong oxidants and especially O_2 are potentially explosive! Proper safety precautions should always be implemented!* This catalytic setup has the advantage that potentially explosive mixtures of molecular oxygen and gaseous hydrocarbons can be avoided. Furthermore, the undesired formation of water as a byproduct in the C−H activation process, which typically inhibits electrophilic catalysts,[65] can possibly be avoided. On the contrary, side reactions by the redox mediator and the two catalysts have to be controlled and an efficient recycling of the redox mediator has to be guaranteed.

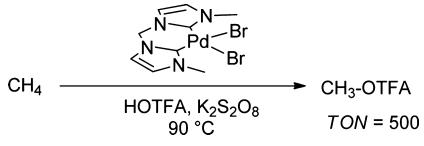
Scheme 1. O_2 and C−H Activation Cycles Coupled by a Redox Mediator



A redox mediator can help to connect these two catalytic events.[66,67] An example for such a process is the C−H functionalization of alkanes by palladium bis(N-heterocyclic carbene) [bis(NHC)] catalysts with bromido ligands in the presence of O_2 and $NaVO_3$.[68−70] Thereby, a palladium(II) catalyst activates the hydrocarbon to form an organometallic intermediate (CH Activation, Scheme 1), whereas an oxovanadium catalyst reacts with the terminal oxidant O_2 (O_2 Activation, Scheme 1). However, without the presence of bromide in the reaction mixture, no turnover is observed. Consequently, it is proposed that the bromide/bromine redox couple (Redox Mediator, Scheme 1) is necessary for coupling O_2 with C−H activation, leading finally to formation of the oxyfunctionalized product methanol.

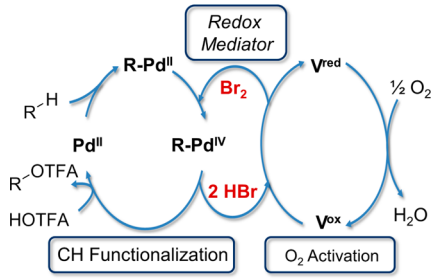
Palladium catalysts with a chelating bis(NHC) ligand like dibromo(1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene)palladium(II) (**1**)[71] were already shown in 2002 to be active catalysts for the functionalization of methane to methyl trifluoroacetate in trifluoroacetic acid (HOTFA) using $K_2S_2O_8$ as the stoichiometric oxidant (Scheme 2).[72] Methyl trifluoroacetate thereby constitutes an electron-poor methyl derivative, which is protected from overoxidation and could, in principle, be hydrolyzed to afford methanol. Complex **1** was originally reported[72] to afford 30 turnovers at 90 °C, although under optimized conditions, a turnover number (TON) of approximately 500 was later demonstrated (Scheme 2).[73]

Scheme 2. Functionalization of Methane by Palladium Bis(NHC) Catalyst 1



Recently, we have shown that halogens can be used as redox mediators in the aerobic, partial oxidation of propane to propyl trifluoroacetates in HOTFA.[68−70] Halogens like chlorine or bromine appear to be good candidates for efficient redox catalysts because they are strong enough oxidants for C−H functionalization chemistry and are well-known to be capable of generating transition-metal complexes in high oxidation states like palladium(IV) or copper(III) by a nonradical two-electron process (Scheme 3).[74−81]

Scheme 3. Coupling of C−H Functionalization by a Palladium Catalyst with Oxovanadium-Catalyzed O_2 Activation



Using a palladium(II) catalyst with chelating bis(NHC) ligands and $NaVO_3$ as the cocatalyst for O_2 activation,[82−91] a TON of over 60 could be demonstrated for the oxidation of propane to isopropyl trifluoroacetate[68] and also the catalytic performance for the conversion of methane to methyl trifluoroacetate.[92] In the case of propane, allyl trifluoroacetate, isopropyl bromide, *n*-propyl trifluoroacetate, and acetone were also formed as minor byproducts. It was shown using radical-transfer reagents that alkyl radicals are not part of the reaction mechanism.[68] Unfortunately, the reaction with methane is extremely slow, and decomposition of the palladium catalyst seems to be an issue.

Very remarkably, however, the reaction with propane does not yield any product without the concomitant presence of a palladium catalyst and bromide, even if using $K_2S_2O_8$ as the final oxidant (vide infra for background reaction in the presence of bromide salts). In the case of methane, traces of bromide in the reaction vessel seem to be enough to lead to efficient catalysis.[93] The presence of molecular bromine in the reaction mixture is clearly visible, the oxidation of organometallic palladium complexes by peroxodisulfate is slow,[70,94,95] and it has also been shown that bromine and chlorine are capable of oxidizing bis(NHC) complexes of palladium and platinum.[63,80,96−98] Accordingly, the presence of bromine appears to be necessary for an efficient oxidation reaction. The reactivity of bromine with palladium complexes with chelating bis(NHC) ligands has also been studied in detail by density functional theory (DFT).[99]

The proposed mechanism for the functionalization of methane, as rationalized by DFT calculations, is shown in Figure 2.[70] According to the DFT calculations [B3LYP-D3(SCRF)/6-311-G(d,p)//B3LYP/6-31-G(d)], the C−H activation step constitutes the rate-determining step ($\Delta G^{\ddagger}$ = 23.4 kcal mol^{-1}) of the mechanism with an overall transition state energy of $\Delta G^{\ddagger}$ = 39.5 kcal mol^{-1}, although the overall

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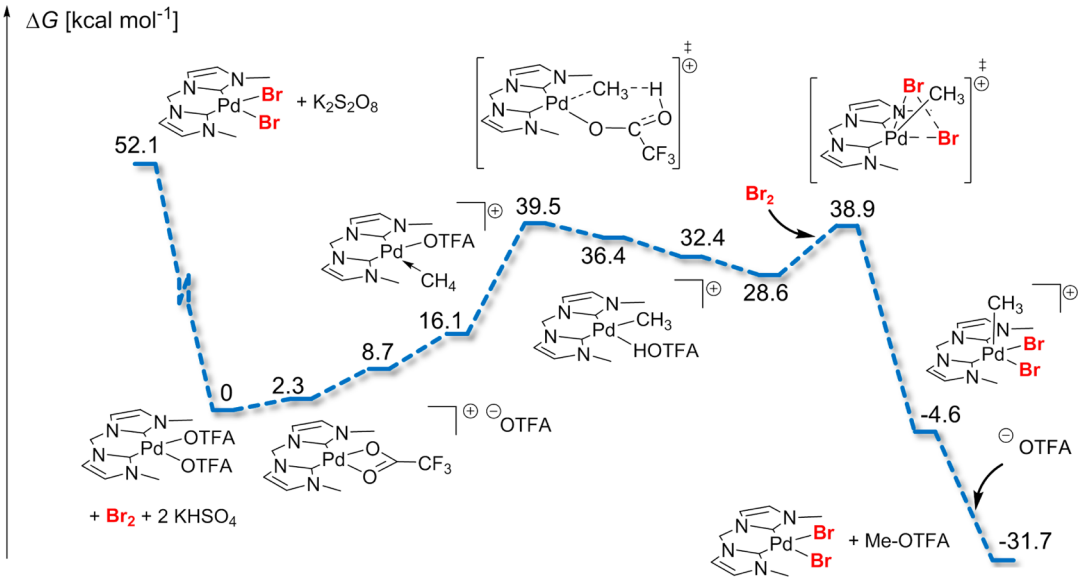

Figure 2. Proposed mechanism[100] for the functionalization of methane by palladium catalysts with chelating bis(NHC) ligands in HOTFA.

transition state energy for the oxidation by bromine is of a similar order of magnitude ($\Delta G^{\ddagger}$ = 38.9 kcal mol^{-1}).

The first step of the proposed mechanism is an oxidative counterligand exchange of the bromido ligands for the relatively weakly coordinating trifluoroacetates by persulfate. This leads to the formation of molecular bromine. Consecutively, a cationic intermediate forms (ΔG = +2.3 kcal mol^{-1}), which coordinates methane in the form of a σ complex (ΔG = +16.1 kcal mol^{-1}) after the formation of a compound with a formally vacant coordination site (ΔG = +8.7 kcal mol^{-1}). C−H activation takes place by an intramolecular deprotonation pathway (electrophilic substitution, concerted metalation - deprotonation) by the trifluoroacetato ligand ($\Delta G^{\ddagger}$ = 39.5 kcal mol^{-1}) and affords a HOTFA-coordinating intermediate (ΔG = 36.4 kcal mol^{-1}).[101,102] Notably, the synthesis and reactivity of a very close analogue has been reported by Subramanium and Slaughter.[103] The oxidation step is mediated by bromine ($\Delta G^{\ddagger}$ = +38.9 kcal mol^{-1}) and leads to the formation of a labile organometallic palladium(IV) species (ΔG = −4.6 kcal mol^{-1}), which reductively eliminates methyl trifluoroacetate without a considerable reaction barrier (ΔG = −31.7 kcal mol^{-1}).

The mechanism for propane is, in principle, equivalent with the C−H activation step also being rate-determining. However, as intermediate β-hydride elimination becomes feasible, isomerization of the *n* to the *iso* isomer is believed to occur between C−H activation and the oxidation step by bromine.[69,99] For the partial oxidation of ethane in sulfuric acid by dipyrimidine platinum complexes, a similar mechanistic picture was drawn,[104] which had previously also been used to explain the trifluoroacetoxylation of sp^3-hybridized methylene groups of alkyl esters, albeit under the intermediate formation of a five-membered palladacycle.[105]

We reasoned that the acidic methylene bridge of the bis(NHC) ligands might be one cause for decomposition of the catalysts. Indeed, substitution of the methylene by an ethylene or *o*-phenylene bridge afforded slightly better or very similar catalytic results.[106,107] Increasing the steric bulk of the wingtip substituents,[107,108] substitution of one NHC ligand by a pyrimidyl moiety,[109] or exchange of the palladium metal for platinum[110] only led to reduced catalytic activity. DFT calculations indicated that most likely the bis(NHC) complex serendipitously employed in the very first report is very close to the intrinsic reactivity maximum for this type of ligand design, with the rate-determining step of the overall catalytic cycle being the C−H activation step.[69] Consequently, more active palladium catalysts with a different enough ligand design are sought. One approach might be the synthesis of bimetallic catalysts, in which the two palladium centers are in close proximity to each other in order to be able to engage in the cooperative activation of a small molecule like methane. Cooperative, bimetallic activation of small molecules is a very well-known concept in catalysis.[111−120] Nevertheless, the two metal centers need to be distant enough from each other to avoid the formation of supposedly inactive Pd−Pd dimers for this kind of reactivity.[75,121] Very recently, we reported the synthesis of a bimetallic, organometallic complex (Figure 3),

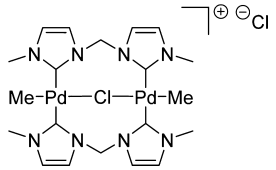

Figure 3. Synthesized potential intermediate.

which raises the question of whether such binuclear species form during the course of methane functionalization.[122] It has also been shown that chelating palladium(II) bis(NHC) complexes can form Pd^{I}−Pd^{I} dimers under reductive conditions.[123]

Lin and Sen had already shown in 1992 that hydrogen peroxide (H_2O_2) can be employed as a redox mediator for the palladium(II)-catalyzed conversion of methane to formic acid under aerobic conditions in the presence of carbon monoxide (CO) and water.[124] Different from the mechanism based on the Br_2/Br^- redox couple as proposed in Scheme 3, the intermediate oxidant H_2O_2 is, however, not regenerated. Later work revealed that the addition of $CuCl_2$ led to the preferential formation of methanol instead of formic acid.[125] The broad application of formic acid for energy storage has

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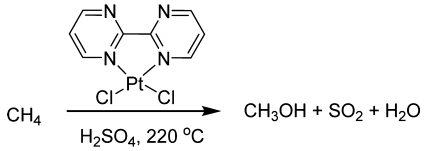
been suggested.[126−128] Although methanol stores more chemical energy than the higher oxidized formic acid, it has been claimed that electricity is generated more efficiently in a fuel cell using formic acid.[129−133]

In this system, hydrogen forms according to the water gas shift reaction involving the reductant CO in reaction with water. Hydrogen then reacts with O_2 and generates H_2O_2. This concept of adding a coreactant like CO or H_2 in order to finally produce H_2O_2 by reaction with oxygen has been applied by several groups.[134−143] Likewise, it was shown that *N*-hydroxyphthalimide, aldehydes, or ethers can serve as coreductants for the formation of H_2O_2.[66,144−148] However, the application of H_2O_2 as an intermediate oxidant hardly can be considered an economically viable route as long as its formation is based on the conversion of methane to syngas or the addition of sacrificial coreductants. Furthermore, the elucidation of mechanisms involving peroxo compounds is often very challenging because they not only oxidize transition-metal compounds very efficiently but also can react with hydrocarbons by single-electron-transfer mechanisms without direct involvement of the transition-metal catalyst.[149−163] A more useful approach could be the application of nitrite/nitrate cooxidants or benzoquinone, which were also shown to be oxidation mediators in the presence of oxygen in the context of alkane activation chemistry.[140,143,164−166] Also, polyoxo cocatalysts, which are capable of both C−H and O_2 activation, have been proven to be promising alternatives.[2,139,167−175]

A similar cooxidation concept could, in principle, also be applied to Periana's platinum(II) system in oleum, which is considered to be a promising system in terms of the methane functionalization activity with a claimed turnover frequency of 0.001 s^{-1} at 90% selectivity (Scheme 4).[176]

Scheme 4. Periana's System for Methane to Methanol Conversion in Sulfuric Acid



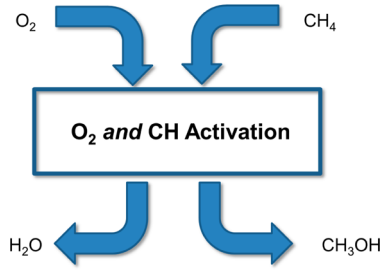
Because oleum is produced by the aerobic oxidation of sulfur dioxide in the presence of a vanadium(V) catalyst (contact process), the partial oxidation of methane could be coupled to this cooxidation using sulfur trioxide as the redox mediator. Similar to the catalytic processes in HOFTA,[68,165,177] however, a drawback is the formation of the byproduct water, which renders the development of an economic process challenging. This might have kept the authors from demonstrating the possibility for an aerobic cooxidation procedure. The mechanism of the Periana system has been studied in depth[65,104,178−180] and has also been reviewed.[16,30]

■ ALKANE FUNCTIONALIZATION AND OXYGEN ACTIVATION BY COBALT CATALYSTS

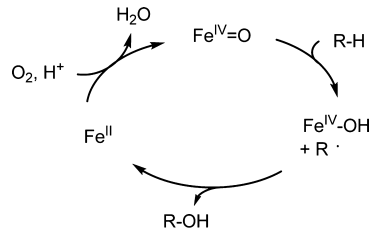
In the second scenario, the same metal compound that functionalizes the hydrocarbon also reacts with the oxidant O_2 (Scheme 5).

A prominent example for this catalytic modus operandi is the oxygen-rebound mechanism of transition-metal oxo compounds, as proposed for cytochrome P450[44,181−190] (Scheme 6) or the oxidation of methane by permanganate.[187]

Scheme 5. O_2 and C−H Activation Taking Place at the Same Catalyst



Scheme 6. Simplified Mechanism for Alkane Functionalization by Cytochrome P450[190]

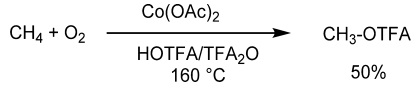


In the case of cytochrome P450, which contains iron in its active site, oxidation of the transition metal affords an iron(IV) oxo intermediate, which reacts with a C−H bond by a radical hydrogen abstraction pathway. Oxygen rebound to the alkyl radical affords the alcohol and regenerates the iron(II) compound. Another example for this type of reactivity might be the reactivity of cobalt compounds in the oxidation states III + or IV+, which will be discussed below in more detail.

The design of catalysts that are capable of both reacting with hydrocarbons and oxygen is a very elegant approach for combining the C−H functionalization of methane with an aerobic oxidation. Typically, this concept involves the net insertion of one oxygen atom into the metal−carbon atom bond by either a radical or a nonradical pathway and therefore often implies the formation of metal oxo complexes.[191−194] This stands in contrast to the Shilov system or the mechanism depicted in Figure 2, where the oxygen atom that is being attached to the methyl carbon atom is derived from the solvent. Most prominent in the literature are arguably iron oxo complexes for the hydroxylation of C−H bonds.[182,185,189,195−199] However, despite encouraging progress in the field of stoichiometric reactivity,[60,200−205] examples of catalytic turnover with methane remain very scarce, and catalyst decomposition seems to be a common issue. Exceptions are homogeneous cobalt and manganese catalysts.[165,177,206−208] Notably, for the aerobic oxidation of cyclohexane to cyclohexanol and cyclohexanone, cobalt catalysts are used in the industry.[209,210]

Cobalt(II) or cobalt(III) salts functionalize methane very efficiently in HOFTA in the presence of O_2 (Scheme 7).[165,207,208] The usage of nitrate as a counterion of cobalt

Scheme 7. Aerobic Functionalization of Methane by Cobalt Salts[165]



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salts leads to exceedingly reactive catalysts. The observation of C−C bond scission processes in the reaction with propane points toward a reaction mechanism involving radicals.[206] One drawback is the incompatibility of the catalysts with water, which forms upon esterification of methane with the acidic solvent.[165,211] Deactivation of the catalyst can be prevented by the addition of trifluoroacetic anhydride; however, once all of trifluoroacetic anhydride is consumed, the catalyst precipitates in the form of cobalt fluorides.

It is very worth noting that cobalt compounds have been known for a long time to be very active in the oxidation of C−H bonds.[212−219] Tang and Kochi already reported in 1973 that cobalt(III) reacts instantaneously at room temperature in HOFTA with alkanes like cyclohexane.[219] It has been described that the aerobic oxidation of hydrocarbons by cobalt(III) compounds can involve the formation of peroxo complexes, whose decomposition yields oxygen-based radicals that initiate radical-based processes.[212] However, others reported on the intermediacy of cobalt(IV) species[220−223] or cobalt(III) high-spin complexes[224,225] for C−H activation reactivity and cobalt(I) pincer complexes for the oxidative addition of C−H bonds.[226,227]

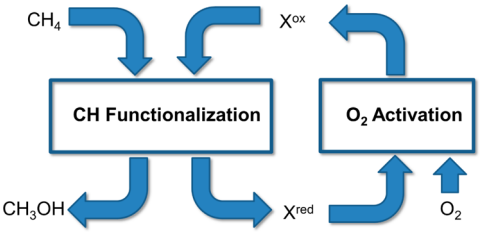
Organometallic compounds can also directly react with O_2; i.e., the C−H activation step can take place before the oxidation step. The oxidation of copper−, palladium−, and platinum−hydrocarbon bonds with oxygen has been reported.[67,200,201,228−235] Goldberg and co-workers, for example, demonstrated that a palladium(II) methyl complex inserts O_2 in the Pd−Me bond by a radical pathway via an intermediate palladium(III) compound to afford a Pd−OOMe complex.[201] Similarly, Britovsek and co-workers suggested the intermediacy of dinuclear triplet states for the light-driven net insertion of O_2 in the metal−Me bond of palladium(II) and platinum(II) pincer complexes.[234] In the case of Vedernikov's dipyridine-ligated platinum complexes, the key to aerobic oxyfunctionalization seems to be the formation of a hydroperoxoplatinum(IV) intermediate, which is proposed to be stabilized by coordination of a sulfonate group attached to the ligand.[232] Undoubtedly a very elegant approach, this catalytic design intrinsically suffers from the concomitant presence of O_2 and hydrocarbon in the same reactor and is sometimes associated with the challenging design of specific ligands.

■ ALKANE FUNCTIONALIZATION MEDIATED BY GROUP XVII OXIDANTS

The application of transition-metal compounds for C−H activation of hydrocarbon C−H bonds is in many ways appealing because ligand- or transition-metal-dictated chemoselectivity can be, in principle, designed. However, homogeneous transition-metal catalysts are typically costly to produce and often suffer from deactivation phenomena. Therefore, cheap main-group compounds like halogens or halide oxo compounds seem to be perfectly suited for the development of a competitive industrial process as long as the challenges of chemoselectivity and overoxidation can be addressed.[3] In any case, also radical mechanisms could be suitable for such an oxidation procedure as long as the primary oxidation product can be trapped, for example, as electron-poor trifluoroacetic acid ester or sulfuric acid ester. Examples for a successful aerobic implementation of this type of approach are rare because often the oxidation potential of molecular oxygen is not high enough to generate the strong intermediate oxidant required, like, for example, peroxodisulfate.

The third approach therefore involves the reaction of a hydrocarbon with a stoichiometric amount of an abundant and cheap oxidant without the help of a transition-metal catalyst (Scheme 8). This oxidant could then be regenerated by an aerobic oxidation protocol.

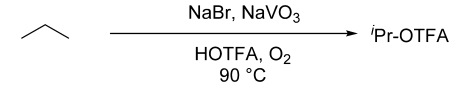
Scheme 8. Alkane Functionalization with a Cheap and Abundant Main-Group Oxidant That Could Be Regenerated by Molecular Oxygen



Especially attractive for the development of halide-based chemical processes for alkane functionalization is the fact that the implementation of aerobic cooxidation procedures could be easier than that for processes involving late transition metals.

We could observe that the presence of sodium bromide also led to the formation of minor amounts of propyl trifluoroacetate with $NaVO_3$ under 4 bar of molecular oxygen and 6 bar of propane without the addition of any transition-metal catalyst (Scheme 9).[68,69] Very remarkably, no formation of *n*-

Scheme 9. Aerobic Partial Oxidation of Propane Provided by the Presence of NaBr



functionalized product was detected. Considering the previous reports on the activation of methane by supposedly Br^+ and I^+ species and that such types of catalytic systems should be extraordinarily robust with regard to demanding reaction conditions, the development of appropriate and more efficient aerobic cooxidation protocols for methane should become feasible in the near future.

The investigation of the reactivity of sodium bromide with propane with the model oxidant peroxodisulfate revealed that the reaction is highly dependent on the concentration of bromide salt.[69] Whereas no product formation (within the margin of error) was determined without the addition of bromide and at a $NaBr/K_2S_2O_8$ ratio of 2:1, the highest yield (53% based on oxidant) was obtained at a 1:1 ratio at 60 °C after 17 h of reaction time. The reaction proceeded with extraordinary cleanliness, and no formation of any byproduct (with the exception of 10% isopropyl bromide) was determined. Consequently, a radical mechanism appears unlikely for this reaction.

The intermediate formation of a haloalkane like methyl bromide prior to an oxyfunctionalization step was already proposed in the 1980s by Olah.[236] Later it was reported that iodine catalyzes the esterification of methane to methyl sulfate in oleum and catalyzes the comproportionation reaction of methane with dibromomethane.[237−240] Also, polyhalomethanes have been shown to be highly active for the activation of hydrocarbon C−H bonds.[33] It was proposed that I^+ species

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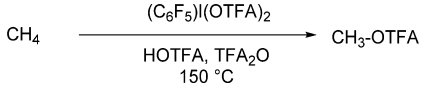
could constitute the catalytically potent intermediate of an electrophilic activation pathway because bromide salts were revealed to be less active and chloride salts were found to be completely inactive.[238] Other reports favor mechanisms involving hypervalent iodine(III) species.[241,242]

Accordingly, a nonradical mechanism has been proposed for the conversion of methane, ethane, and propane by a defined iodine(III) complex (Scheme 10).[242]

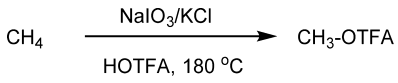
Scheme 10. Selective Partial Methane Oxidation by an Iodine(III) Compound



However, modes of reactivity have to be considered to be fluent from radical-dominated or single-electron-transfer chemistry to mainly electrophilic-type behaviors and parallels to "Olah-type" chemistry in the presence of superacids are evident.[34,35,236,243,244] In any case, conducting the reaction in strong acids typically leads to the formation of electron-poor esters, which are protected from further oxidation.[69,245]

Gunnoe and co-workers discovered that iodate salts convert methane to methyl trifluoroacetate in HOFTA if a source of chloride is present (Scheme 11).[245]

Scheme 11. Stoichometric Conversion of Methane to Methyl Trifluoroacetate by Iodates



The reaction proceeds with very high chemoselectivity (>85%) for methyl trifluoroacetate, and yields of over 20% based on methane were demonstrated after a reaction time of only 1 h. Remarkably, iodates form under acidic conditions by reaction with O_2.[246] Consequently, it could be envisioned to regenerate the oxidant iodate by such an aerobic cooxidation procedure. Very recently, it was shown that substituting iodate by periodate leads to even higher yields of up to 42%.[247] In the reaction with propane, $NaIO_4$/KCl showed a higher selectivity for functionalizing the *iso* position (*iso*:*n* = 2.6:1) than $NaIO_3$/KCl (*iso*:*n* = 1.7:1). In a distinction to the iodate system, chlorinated byproducts formed in considerable yield, as exemplified by the reaction with ethane ($NaIO_4$/KCl, EtOTFA:EtCl = 3.3:1; $NaIO_3$/KCl, EtOTFA:EtCl = 16:1).

CONCLUSION

Reported catalytic systems for the partial oxidation of methane typically suffer from the usage of expensive oxidants, low catalytic activity, and catalyst deactivation. Therefore, three approaches toward the development of aerobic oxidation procedures have been discussed that address the mentioned challenges. These include (1) the application of redox mediators like halogens between a late-transition-metal C−H functionalization catalyst and an early-transition-metal catalyst for O_2 activation, (2) cobalt catalysts, which have been shown to functionalize methane using O_2 as oxidant directly, and (3) the development of very robust and cheap group XVII main-group oxidants for the functionalization of methane and lower hydrocarbons like propane.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Worldbank, http://go.worldbank.org/016TLXI7N0, accessed March 6, 2015.
(2) Sun, M.; Zhang, J. Z.; Putaj, P.; Caps, V.; Lefebvre, F.; Pelletier, J.; Basset, J. M. *Chem. Rev.* **2014**, *114*, 981−1019.
(3) Hammond, C.; Conrad, S.; Hermans, I. *ChemSusChem* **2012**, *5*, 1668−1686.
(4) Surya Prakash, G. K.; Olah, G. A. *Isr. J. Chem.* **2014**, *54*, 1412−1412.
(5) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174−2175.
(6) Gol'dshleger, N. F.; Khidekel, M. L.; Shilov, A. E.; Shteinman, A. A. *Kinet. Katal.* **1974**, *15*, 261−263.
(7) Shilov, A. E.; Shulpin, G. B. *Activation and catalytic reactions of saturated hydrocarbons in the presence of metal complexes*; Kluwer Academic: Dordrecht, The Netherlands, 2002.
(8) Cavaliere, V. N.; Mindiola, D. J. *Chem. Sci.* **2012**, *3*, 3356−3365.
(9) Pamplin, C. B.; Legzdins, P. *Acc. Chem. Res.* **2003**, *36*, 223−233.
(10) Webb, J. R.; Burgess, S. A.; Cundari, T. R.; Gunnoe, T. B. *Dalton Trans.* **2013**, *42*, 16646−16665.
(11) Waterman, R. *Organometallics* **2013**, *32*, 7249−7263.
(12) Gunay, A.; Theopold, K. H. *Chem. Rev.* **2010**, *110*, 1060−1081.
(13) Baillie, R. A.; Legzdins, P. *Acc. Chem. Res.* **2013**, *47*, 330−340.
(14) Chepaikin, E. G. *Russ. Chem. Rev.* **2011**, *80*, 363−396.
(15) Caballero, A.; Perez, P. J. *Chem. Soc. Rev.* **2013**, *42*, 8809−8820.
(16) Hashiguchi, B. G.; Bischof, S. M.; Konnick, M. M.; Periana, R. A. *Acc. Chem. Res.* **2012**, *45*, 885−898.
(17) Crabtree, R. H. *J. Organomet. Chem.* **2004**, *689*, 4083−4091.
(18) Goldberg, K. I.; Goldman, A. S. *Activation and Functionalization of C−H Bonds*; American Chemical Society: Washington, DC, 2004.
(19) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507−514.
(20) Golisz, S. R.; Gunnoe, T. B.; Goddard, W. A.; Groves, J. T.; Periana, R. A. *Catal. Lett.* **2010**, *141*, 213−221.
(21) Perez, P. J. E. *Alkane C−H Activation by Single-Site Metal Catalysis*; Springer: Dordrecht, The Netherlands, 2012.
(22) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162.
(23) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550−557.
(24) Schwarz, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 10096−10115.
(25) Gol'dshleger, N. F.; Moravskii, A. P. *Russ. Chem. Rev.* **1994**, *63*, 125−138.
(26) Jones, W. D. *Top. Organomet. Chem.* **1999**, *3*, 9−46.
(27) Webb, J. R.; Bolano, T.; Gunnoe, T. B. *ChemSusChem* **2011**, *4*, 37−49.

DOI: 10.1021/ic502515x
Inorg. Chem. 2015, 54, 5043−5052

(28) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633−639.
(29) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471−2526.
(30) Gunsalus, N. J.; Konnick, M. M.; Hashiguchi, B. G.; Periana, R. A. *Isr. J. Chem.* **2014**, *54*, 1467−1480.
(31) Schwarz, H. *Isr. J. Chem.* **2014**, *54*, 1413−1431.
(32) Hashiguchi, B. G.; Konnick, M. M.; Bischof, S. M.; Gustafson, S. J.; Devarajan, D.; Gunsalus, N.; Ess, D. H.; Periana, R. A. *Science* **2014**, *343*, 1232−1237.
(33) Akhrem, I.; Orlinkov, A. *Chem. Rev.* **2007**, *107*, 2037−2079.
(34) Olah, G. A.; Prakash, G. K. S. *Electrophilic Reactions of Alkanes. The Chemistry of Alkanes and Cycloalkanes*; John Wiley & Sons Ltd.: Chichester, U.K., 2006.
(35) Fokin, A. A.; Schreiner, P. R. *Chem. Rev.* **2002**, *102*, 1551−1594.
(36) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91.
(37) Caballero, A.; Despagnet-Ayoub, E.; Diaz-Requejo, M. M.; Diaz-Rodriguez, A.; Gonzalez-Nunez, M. E.; Mello, R.; Munoz, B. K.; Ojo, W. S.; Asensio, G.; Etienne, M.; Perez, P. J. *Science* **2011**, *332*, 835−838.
(38) Bissinger, P.; Braunschweig, H.; Damme, A.; Dewhurst, R. D.; Kupfer, T.; Radacki, K.; Wagner, K. *J. Am. Chem. Soc.* **2011**, *133*, 19044−19047.
(39) Prechtl, M. H.; Teltewskoi, M.; Dimitrov, A.; Kemnitz, E.; Braun, T. *Chem.—Eur. J.* **2011**, *17*, 14385−14388.
(40) Groves, J. T. *Nat. Chem.* **2014**, *6*, 89−91.
(41) Yosca, T. H.; Rittle, J.; Krest, C. M.; Onderko, E. L.; Silakov, A.; Calixto, J. C.; Behan, R. K.; Green, M. T. *Science* **2013**, *342*, 825−829.
(42) Shilov, A. E.; Shteinman, A. A. *Russ. Chem. Rev.* **2012**, *81*, 291−316.
(43) Fasan, R. *ACS Catal.* **2012**, *2*, 647−666.
(44) Meunier, B.; de Visser, S. P.; Shaik, S. *Chem. Rev.* **2004**, *104*, 3947−3980.
(45) Lewis, J. C.; Coelho, P. S.; Arnold, F. H. *Chem. Soc. Rev.* **2011**, *40*, 2003−2021.
(46) Lieberman, R. L.; Rosenzweig, A. C. *Nature* **2005**, *434*, 177−182.
(47) Basch, H.; Mogi, K.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1999**, *121*, 7249−7256.
(48) Austin, R. N.; Groves, J. T. *Metallomics* **2011**, *3*, 775−787.
(49) Balasubramanian, R.; Rosenzweig, A. C. *Acc. Chem. Res.* **2007**, *40*, 573−580.
(50) Stoukides, M. *J. Appl. Electrochem.* **1995**, *25*, 899−912.
(51) Baltrusaitis, J.; Jansen, I.; Christus, J. D. S. *Catal. Sci. Technol.* **2014**, *4*, 2397−2411.
(52) Murray, E. P.; Tsai, T.; Barnett, S. A. *Nature* **1999**, *400*, 649−651.
(53) Manohar, A. K.; Narayanan, S. R. *Isr. J. Chem.* **2014**, *54*, 1443−1450.
(54) Chepaikin, E. G. *J. Mol. Catal. A: Chem.* **2014**, *385*, 160−174.
(55) Periana, R. A.; Bhalla, G.; Tenn, W. J.; Young, K. J. H.; Liu, X. Y.; Mironov, O.; Jones, C.; Ziatdinov, V. R. *J. Mol. Catal. A: Chem.* **2004**, *220*, 7−25.
(56) Labinger, J. A. *J. Mol. Catal. A: Chem.* **2004**, *220*, 27−35.
(57) Roduner, E.; Kaim, W.; Sarkar, B.; Urlacher, V. B.; Pleiss, J.; Glaser, R.; Einicke, W. D.; Sprenger, G. A.; Beifuss, U.; Klemm, E.; Liebner, C.; Hieronymus, H.; Hsu, S. F.; Plietker, B.; Laschat, S. *ChemCatChem* **2013**, *5*, 82−112.
(58) Ess, D. H.; Goddard, W. A.; Periana, R. A. *Organometallics* **2010**, *29*, 6459−6472.
(59) Topczewski, J. J.; Sanford, M. S. *Chem. Sci.* **2015**, *6*, 70−76.
(60) Mei, J. J.; Carsch, K. M.; Freitag, C. R.; Gunnoe, T. B.; Cundari, T. R. *J. Am. Chem. Soc.* **2013**, *135*, 424−435.
(61) Figg, T. M.; Webb, J. R.; Cundari, T. R.; Gunnoe, T. B. *J. Am. Chem. Soc.* **2012**, *134*, 2332−2339.
(62) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025−8032.
(63) McCall, A. S.; Wang, H.; Desper, J. M.; Kraft, S. *J. Am. Chem. Soc.* **2011**, *133*, 1832−1848.
(64) Kaizer, J.; Klinker, E. J.; Oh, N. Y.; Rohde, J.-U.; Song, W. J.; Stubna, A.; Kim, J.; Münck, E.; Nam, W.; Que, L. *J. Am. Chem. Soc.* **2003**, *126*, 472−473.
(65) Ahlquist, M.; Periana, R. A.; Goddard, W. A. *Chem. Commun.* **2009**, 2373−2375.
(66) Clerici, M. G.; Ingallina, P. *Catal. Today* **1998**, *41*, 351−364.
(67) Campbell, A. N.; Stahl, S. S. *Acc. Chem. Res.* **2012**, *45*, 851−863.
(68) Munz, D.; Strassner, T. *Angew. Chem., Int. Ed.* **2014**, *53*, 2485−2488.
(69) Munz, D.; Strassner, T. *Chem.—Eur. J.* **2014**, *20*, 14872−14879.
(70) Munz, D.; Meyer, D.; Strassner, T. *Organometallics* **2013**, *32*, 3469−3480.
(71) Herdtweck, E.; Muehlhofer, M.; Strassner, T. *Acta Crystallogr., Sect. E* **2003**, *59*, M970−M971.
(72) Muehlhofer, M.; Strassner, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1745−1747.
(73) Munz, D. Diplomarbeit, TU Dresden, Dresden, Germany, 2009.
(74) Hickman, A. J.; Sanford, M. S. *Nature* **2012**, *484*, 177−185.
(75) Powers, D. C.; Ritter, T. *Acc. Chem. Res.* **2012**, *45*, 840−850.
(76) Chen, X.; Engle, K. M.; Wang, D. H.; Yu, J. Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094−5115.
(77) Canty, A. J. *Dalton Trans.* **2009**, 10409−10417.
(78) Xu, L. M.; Li, B. J.; Yang, Z.; Shi, Z. J. *Chem. Soc. Rev.* **2010**, *39*, 712−733.
(79) Vedernikov, A. N.; Kuramshin, A. I.; Solomonov, B. N. *J. Chem. Soc., Chem. Commun.* **1994**, 121−122.
(80) Rivada-Wheelaghan, O.; Ortuno, M. A.; Diez, J.; Garcia-Garrido, S. E.; Maya, C.; Lledos, A.; Conejero, S. *J. Am. Chem. Soc.* **2012**, *134*, 15261−15264.
(81) Engle, K. M.; Mei, T. S.; Wang, X.; Yu, J. Q. *Angew. Chem., Int. Ed.* **2011**, *50*, 1478−1491.
(82) Kikushima, K.; Moriuchi, T.; Hirao, T. *Tetrahedron* **2010**, *66*, 6906−6911.
(83) Kikushima, K.; Moriuchi, T.; Hirao, T. *Tetrahedron Lett.* **2010**, *51*, 340−342.
(84) Moriuchi, T.; Kikushima, K.; Kajikawa, T.; Hirao, T. *Tetrahedron Lett.* **2009**, *50*, 7385−7387.
(85) Kikushima, K.; Moriuchi, T.; Hirao, T. *Chem.—Asian J.* **2009**, *4*, 1213−1216.
(86) Simandi, L. *Catalytic Activation of Dioxygen by Metal Complexes*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992.
(87) Licini, G.; Conte, V.; Coletti, A.; Mba, M.; Zonta, C. *Coord. Chem. Rev.* **2011**, *255*, 2345−2357.
(88) da Silva, J. A. L.; da Silva, J. J. R. F.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **2011**, *255*, 2232−2248.
(89) Cozzolino, A. F.; Tofan, D.; Cummins, C. C.; Temprado, M.; Palluccio, T. D.; Rybak-Akimova, E. V.; Majumdar, S.; Cai, X.; Captain, B.; Hoff, C. D. *J. Am. Chem. Soc.* **2012**, *134*, 18249−18252.
(90) Waidmann, C. R.; DiPasquale, A. G.; Mayer, J. M. *Inorg. Chem.* **2010**, *49*, 2383−2391.
(91) Egdal, R. K.; Bond, A. D.; McKenzie, C. J. *Dalton Trans.* **2009**, 3833−3839.
(92) Munz, D.; Strassner, T. Unpublished work.
(93) Strassner, T.; Muehlhofer, M.; Zeller, A.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.* **2004**, *689*, 1418−1424.
(94) Borduas, N.; Lough, A. J.; Dong, V. M. *Inorg. Chim. Acta* **2011**, *369*, 247−252.
(95) Gary, J. B.; Cook, A. K.; Sanford, M. S. *ACS Catal.* **2013**, *3*, 700−703.
(96) Meyer, D.; Ahrens, S.; Strassner, T. *Organometallics* **2010**, *29*, 3392−3396.
(97) Khlebnikov, V.; Heckenroth, M.; Muller-Bunz, H.; Albrecht, M. *Dalton Trans.* **2013**, *42*, 4197−4207.
(98) Alsters, P. L.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Spek, A. L.; Koten, G. v. *Organometallics* **1993**, *12*, 1831−1844.
(99) Munz, D.; Strassner, T. *Top. Catal* **2014**, 1−5.
(100) The reaction barrier seems to be too high but includes charge separation and is mainly due to the challenges regarding the solvent treatment for the formation of the cationic, methane-coordinating σ

DOI: 10.1021/ic502515x
Inorg. Chem. 2015, 54, 5043−5052

complex. It is discussed in detail in: Munz, D.; Meyer, D.; Strassner, T. *Organometallics* **2013**, *32*, 3469−3480.
(101) Balcells, D.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2010**, *110*, 749−823.
(102) Boutadla, Y.; Davies, D. L.; Macgregor, S. A.; Poblador-Bahamonde, A. I. *Dalton Trans.* **2009**, 5820−5831.
(103) Subramanium, S. S.; Slaughter, L. M. *Dalton Trans.* **2009**, 6930−6933.
(104) Konnick, M. M.; Bischof, S. M.; Yousufuddin, M.; Hashiguchi, B. G.; Ess, D. H.; Periana, R. A. *J. Am. Chem. Soc.* **2014**, *136*, 10085−10094.
(105) Hou, X.-F.; Wang, Y.-N.; Göttker-Schnetmann, I. *Organometallics* **2011**, *30*, 6053−6056.
(106) Ahrens, S.; Zeller, A.; Taige, M.; Strassner, T. *Organometallics* **2006**, *25*, 5409−5415.
(107) Munz, D.; Poethig, A.; Tronnier, A.; Strassner, T. *Dalton Trans.* **2013**, *42*, 7297−7304.
(108) Ahrens, S. Imidazoliumsalze: Liganden in stabile Biscarbenkatalysatoren für die CH-Aktivierung von Methan und neuartige ionische Flüssigkeiten. Dissertation, München, Germany, 2008.
(109) Meyer, D.; Taige, M. A.; Zeller, A.; Hohlfeld, K.; Ahrens, S.; Strassner, T. *Organometallics* **2009**, *28*, 2142−2149.
(110) Ahrens, S.; Strassner, T. *Inorg. Chim. Acta* **2006**, *359*, 4789−4796.
(111) Feringa, B. L.; van den Beuken, E. K. *Tetrahedron* **1998**, *54*, 12985−13011.
(112) Uyeda, C.; Peters, J. C. *Chem. Sci.* **2013**, *4*, 157.
(113) Hetterscheid, D. G. H.; van der Vlugt, J. I.; de Bruin, B.; Reek, J. N. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 8178−8181.
(114) Fafard, C. M.; Adhikari, D.; Foxman, B. M.; Mindiola, D. J.; Ozerov, O. V. *J. Am. Chem. Soc.* **2007**, *129*, 10318−10319.
(115) van der Vlugt, J. I. *Eur. J. Inorg. Chem.* **2012**, *2012*, 363−375.
(116) Fout, A. R.; Basuli, F.; Fan, H.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 3291−3295.
(117) Sola, E.; Bakhmutov, V. I.; Torres, F.; Elduque, A.; López, J. A.; Lahoz, F. J.; Werner, H.; Oro, L. A. *Organometallics* **1998**, *17*, 683−696.
(118) Mata, J. A.; Hahn, F. E.; Peris, E. *Chem. Sci.* **2014**, *5*, 1723−1732.
(119) Velian, A.; Lin, S.; Miller, A. J. M.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2010**, *132*, 6296−6297.
(120) Lin, S.; Herbert, D. E.; Velian, A.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2013**, *135*, 15830−15840.
(121) Powers, D. C.; Lee, E.; Ariafard, A.; Sanford, M. S.; Yates, B. F.; Canty, A. J.; Ritter, T. *J. Am. Chem. Soc.* **2012**, *134*, 12002−12009.
(122) Meyer, D.; Strassner, T. *J. Organomet. Chem.* **2015**, *784*, 84−87.
(123) Boyd, P. D.; Edwards, A. J.; Gardiner, M. G.; Ho, C. C.; Lemee-Cailleau, M. H.; McGuinness, D. S.; Riapanitra, A.; Steed, J. W.; Stringer, D. N.; Yates, B. F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6315−6318.
(124) Lin, M. R.; Sen, A. *J. Am. Chem. Soc.* **1992**, *114*, 7307−7308.
(125) Hogan, T.; Sen, A. *J. Am. Chem. Soc.* **1997**, *119*, 2642−2646.
(126) Boddien, A.; Mellmann, D.; Gartner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurenczy, G.; Ludwig, R.; Beller, M. *Science* **2011**, *333*, 1733−1736.
(127) Ostapowicz, T. G.; Schmitz, M.; Krystof, M.; Klankermayer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2013**, *52*, 12119−12123.
(128) Boddien, A.; Junge, H. *Nat. Nanotechnol.* **2011**, *6*, 265−266.
(129) Loges, B.; Boddien, A.; Junge, H.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3962−3965.
(130) Busse, K.-H. Power Supply System, in particular for the Field of Building Technology. Patent PCT/EP2012/002429, 2013.
(131) Tedsree, K.; Li, T.; Jones, S.; Chan, C. W. A.; Yu, K. M. K.; Bagot, P. A. J.; Marquis, E. A.; Smith, G. D. W.; Tsang, S. C. E. *Nat. Nanotechnol.* **2011**, *6*, 302−307.
(132) Boddien, A.; Loges, B.; Junge, H.; Gärtner, F.; Noyes, J. R.; Beller, M. *Adv. Synth. Catal.* **2009**, *351*, 2517−2520.
(133) Boddien, A.; Loges, B.; Junge, H.; Beller, M. *ChemSusChem* **2008**, *1*, 751−758.
(134) Otsuka, K.; Yamanaka, I.; Wang, Y. *Stud. Surf. Sci. Catal.* **1998**, *119*, 15−24.
(135) Yamanaka, I.; Soma, M.; Otsuka, K. *Res. Chem. Intermediat.* **2000**, *26*, 129−135.
(136) Otsuka, K.; Wang, Y. *Appl. Catal., A* **2001**, *222*, 145−161.
(137) Yamanaka, I.; Hasegawa, S.; Otsuka, K. *Appl. Catal., A* **2002**, *226*, 305−315.
(138) Shen, C. Y.; Garcia-Zayas, E. A.; Sen, A. *J. Am. Chem. Soc.* **2000**, *122*, 4029−4031.
(139) Kuznetsova, N. I.; Kirillova, N. V.; Kuznetsova, L. I.; Likholobov, V. A. *J. Mol. Catal. A: Chem.* **2003**, *204*, 591−597.
(140) Pan, X. L.; Fan, Y. F.; An, Z. J.; Liu, X. M.; Bao, X. H. *Chem. Commun.* **2009**, 7488−7490.
(141) Chepaikin, E. G.; Bezruchenko, A. P.; Leshcheva, A. A.; Boyko, G. N.; Kuzmenkov, I. V.; Grigoryan, E. H.; Shilov, A. E. *J. Mol. Catal. A: Chem.* **2001**, *169*, 89−98.
(142) Park, E. D.; Hwang, Y.-S.; Lee, C. W.; Lee, J. S. *Appl. Catal., A* **2003**, *247*, 269−281.
(143) An, Z. J.; Pan, X. L.; Liu, X. M.; Han, X. W.; Bao, X. H. *J. Am. Chem. Soc.* **2006**, *128*, 16028−16029.
(144) Weinstein, A. B.; Stahl, S. S. *Catal. Sci. Technol.* **2014**, *4*, 4301−4307.
(145) Yan, Y. P.; Feng, P.; Zheng, Q. Z.; Liang, Y. F.; Lu, J. F.; Cui, Y. X.; Jiao, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 5827−5831.
(146) Ishii, Y.; Sakaguchi, S.; Iwahama, T. *Adv. Synth. Catal.* **2001**, *343*, 393−427.
(147) Murahashi, S.; Oda, Y.; Naota, T. *J. Am. Chem. Soc.* **1992**, *114*, 7913−7914.
(148) Goberna-Ferrón, S.; Lillo, V.; Galán-Mascarós, J. R. *Catal. Commun.* **2012**, *23*, 30−33.
(149) Kao, L. C.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991**, *113*, 700−701.
(150) Shulpin, G. B. *Mini-Rev. Org. Chem.* **2009**, *6*, 95−104.
(151) Camaioni, D. M.; Bays, J. T.; Shaw, W. J.; Linehan, J. C.; Birnbaum, J. C. *J. Org. Chem.* **2001**, *66*, 789−795.
(152) Ingrosso, G.; Midollini, N. *J. Mol. Catal. A: Chem.* **2003**, *204*−*205*, 425−431.
(153) Kirillova, M. V.; Kozlov, Y. N.; Shul'pina, L. S.; Lyakin, O. Y.; Kirillov, A. M.; Talsi, E. P.; Pombeiro, A. J. L.; Shul'pin, G. B. *J. Catal.* **2009**, *268*, 26−38.
(154) Kirillova, M. V.; Kirillov, A. M.; Pombeiro, A. J. L. *Chem.—Eur. J.* **2010**, *16*, 9485−9493.
(155) Kirillova, M. V.; Kuznetsov, M. L.; Reis, P. M.; da Silva, J. A.; da Silva, J. J.; Pombeiro, A. J. *J. Am. Chem. Soc.* **2007**, *129*, 10531−10545.
(156) Mizuno, N.; Kamata, K. *Coord. Chem. Rev.* **2011**, *255*, 2358−2370.
(157) Gonzalez Cuervo, L.; Kozlov, Y. N.; Suss-Fink, G.; Shulpin, G. B. *J. Mol. Catal. A: Chem.* **2004**, *218*, 171−177.
(158) Kirillova, M. V.; Kirillov, A. M.; Mandelli, D.; Carvalho, W. A.; Pombeiro, A. J. L.; Shul'pin, G. B. *J. Catal.* **2010**, *272*, 9−17.
(159) MacLeod, T. C. O.; Kirillova, M. V.; Pombeiro, A. J. L.; Schiavon, M. A.; Assis, M. D. *Appl. Catal., A* **2010**, *372*, 191−198.
(160) Kirillova, M. V.; Kirillov, A. M.; Kuznetsov, M. L.; Silva, J. A. L.; da Silva, J. J. R. F.; Pombeiro, A. J. L. *Chem. Commun.* **2009**, 2353−2355.
(161) Kirillova, M.; Kirillov, A.; Reis, P.; Silva, J.; Fraustodasilva, J.; Pombeiro, A. *J. Catal.* **2007**, *248*, 130−136.
(162) Kirillova, M. V.; da Silva, J. A. L.; da Silva, J. J. R. F.; Palavra, A. F.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2007**, *349*, 1765−1774.
(163) Comba, P.; Lee, Y.-M.; Nam, W.; Waleska, A. *Chem. Commun.* **2014**, *50*, 412−414.
(164) Stowers, K. J.; Kubota, A.; Sanford, M. S. *Chem. Sci.* **2012**, *3*, 3192−3195.
(165) Strassner, T.; Ahrens, S.; Muehlhofer, M.; Munz, D.; Zeller, A. *Eur. J. Inorg. Chem.* **2013**, *21*, 3659−3663.

DOI: 10.1021/ic502515x
Inorg. Chem. 2015, 54, 5043−5052

(166) Popp, B. V.; Stahl, S. S. *Top. Organomet. Chem.* **2007**, *22*, 149−189.
(167) Yuan, J.; Wang, L.; Wang, Y. *Ind. Eng. Chem. Res.* **2011**, *50*, 6513−6516.
(168) Bar-Nahum, I.; Khenkin, A. M.; Neumann, R. *J. Am. Chem. Soc.* **2004**, *126*, 10236−10237.
(169) Okamoto, M.; Watanabe, M.; Yamaji, T. *J. Organomet. Chem.* **2002**, *664*, 59−65.
(170) Kuznetsova, N. I.; Kuznetsova, L. I. *Kinet. Catal.* **2009**, *50*, 1−10.
(171) Sun, M.; Abou-Hamad, E.; Rossini, A. J.; Zhang, J. Z.; Lesage, A.; Zhu, H. B.; Pelletier, J.; Emsley, L.; Caps, V.; Basset, J. M. *J. Am. Chem. Soc.* **2013**, *135*, 804−810.
(172) Yuan, J.; Liu, L.; Wang, L.; Hao, C. *Catal. Lett.* **2013**, *143*, 126−129.
(173) Kozhevnikov, I. V. *J. Mol. Catal. A: Chem.* **2007**, *262*, 86−92.
(174) Kitamura, T.; Piao, D.-G.; Taniguchi, Y.; Fujiwara, Y. *Stud. Surf. Sci. Catal.* **1998**, *119*, 301−305.
(175) Fujiwara, Y.; Piao, D.; Inoue, K.; Shibasaki, H.; Taniguchi, Y.; Kitamura, T. *J. Organomet. Chem.* **1999**, *574*, 116−120.
(176) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560−564.
(177) Chen, W.; Kocal, J. A.; Brandvold, T. A.; Bricker, M. L.; Bare, S. R.; Broach, R. W.; Greenlay, N.; Popp, K.; Walenga, J. T.; Yang, S. S.; Low, J. J. *Catal. Today* **2009**, *140*, 157−161.
(178) Mironov, O. A.; Bischof, S. M.; Konnick, M. M.; Hashiguchi, B. G.; Ziatdinov, V. R.; Goddard, W. A.; Ahlquist, M.; Periana, R. A. *J. Am. Chem. Soc.* **2013**, *135*, 14644−14658.
(179) Ahlquist, M.; Nielsen, R. J.; Periana, R. A.; Goddard, W. A. *J. Am. Chem. Soc.* **2009**, *131*, 17110−17115.
(180) Kua, J.; Xu, X.; Periana, R. A.; Goddard, W. A. *Organometallics* **2002**, *21*, 511−525.
(181) Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3103−3113.
(182) Groves, J. T.; Mcclusky, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 859−861.
(183) Groves, J. T. *J. Chem. Educ.* **1985**, *62*, 928−931.
(184) Kamachi, T.; Yoshizawa, K. *J. Am. Chem. Soc.* **2003**, *125*, 4652−4661.
(185) Que, L. *Acc. Chem. Res.* **2007**, *40*, 493−500.
(186) Costas, M.; Chen, K.; Que, L. *Coord. Chem. Rev.* **2000**, *200−202*, 517−544.
(187) Strassner, T.; Houk, K. N. *J. Am. Chem. Soc.* **2000**, *122*, 7821−7822.
(188) Ogliaro, F.; Harris, N.; Cohen, S.; Filatov, M.; de Visser, S. P.; Shaik, S. *J. Am. Chem. Soc.* **2000**, *122*, 8977−8989.
(189) Shaik, S.; Kumar, D.; de Visser, S. P.; Altun, A.; Thiel, W. *Chem. Rev.* **2005**, *105*, 2279−2328.
(190) McQuarters, A. B.; Wolf, M. W.; Hunt, A. P.; Lehnert, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 4750−4752.
(191) Punniyamurthy, T.; Velusamy, S.; Iqbal, J. *Chem. Rev.* **2005**, *105*, 2329−2363.
(192) Zhou, M.; Crabtree, R. H. *Chem. Soc. Rev.* **2011**, *40*, 1875−1884.
(193) Shi, Z. Z.; Zhang, C.; Tang, C. H.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3381−3430.
(194) Lotz, M. D.; Remy, M. S.; Lao, D. B.; Ariafard, A.; Yates, B. F.; Canty, A. J.; Mayer, J. M.; Sanford, M. S. *J. Am. Chem. Soc.* **2014**, *136*, 8237−8242.
(195) Geng, C.; Ye, S.; Neese, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 5717−5720.
(196) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 6243−6248.
(197) Groves, J. T.; Vanderpuy, M. *J. Am. Chem. Soc.* **1976**, *98*, 5290−5297.
(198) Nam, W. *Acc. Chem. Res.* **2007**, *40*, 522−531.
(199) Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, *25*, 504−512.
(200) Boisvert, L.; Goldberg, K. I. *Acc. Chem. Res.* **2011**, *45*, 899−910.
(201) Boisvert, L.; Denney, M. C.; Hanson, S. K.; Goldberg, K. I. *J. Am. Chem. Soc.* **2009**, *131*, 15802−15814.
(202) Pouy, M. J.; Milczek, E. M.; Figg, T. M.; Otten, B. M.; Prince, B. M.; Gunnoe, T. B.; Cundari, T. R.; Groves, J. T. *J. Am. Chem. Soc.* **2012**, *134*, 12920−12923.
(203) Bischof, S. M.; Cheng, M. J.; Nielsen, R. J.; Gunnoe, T. B.; Goddard, W. A.; Periana, R. A. *Organometallics* **2011**, *30*, 2079−2082.
(204) Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 2219−2220.
(205) Alsters, P. L.; Teunissen, H. T.; Boersma, J.; Spek, A. L.; Koten, G. v. *Organometallics* **1993**, *12*, 4691−4696.
(206) Stolarov, I. P.; Vargaftik, M. N.; Shishkin, D. I.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1991**, 938−939.
(207) Vargaftik, M. N.; Stolarov, I. P.; Shishkin, D. I.; Moiseev, I. I. *Teor. Eksp. Khim.* **1991**, *27*, 301−307.
(208) Vargaftik, M. N.; Stolarov, I. P.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1990**, 1049−1050.
(209) Valdez, D. L. Invista Technologies S.A.R.L.: Process for the oxidation of cyclohexane. Patent PCT/US2012/047400, 2014.
(210) Rapoport, M.; White, J. O. E. I. Du Pont De Nemours and Company: Process for the oxidation of cyclohexane. U.S. Patent 3,957,876A, 1976.
(211) Chavez, F. A.; Rowland, J. M.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 9015−9027.
(212) Chavez, F. A.; Mascharak, P. K. *Acc. Chem. Res.* **2000**, *33*, 539−545.
(213) Tang, H.; Shen, C. Y.; Lin, M. R.; Sen, Y. *Inorg. Chim. Acta* **2000**, *300*, 1109−1111.
(214) Asadullah, M.; Taniguchi, Y.; Kitamura, T.; Fujiwara, Y. *Appl. Catal., A* **2000**, *194−195*, 443−452.
(215) Asadullah, M.; Taniguchi, Y.; Kitamura, T.; Fujiwara, Y. *Tetrahedron Lett.* **1999**, *40*, 8867−8871.
(216) Mandal, A. K.; Iqbal, J. *Tetrahedron* **1997**, *53*, 7641−7648.
(217) Ryan, M. F.; Fiedler, A.; Schroeder, D.; Schwarz, H. *Organometallics* **1994**, *13*, 4072−4081.
(218) Goldstein, A. S.; Drago, R. S. *Inorg. Chem.* **1991**, *30*, 4506−4510.
(219) Tang, R.; Kochi, J. K. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3845−3856.
(220) Nguyen, A. I.; Hadt, R. G.; Solomon, E. I.; Tilley, T. D. *Chem. Sci.* **2014**, *5*, 2874−2878.
(221) Pfaff, F. F.; Kundu, S.; Risch, M.; Pandian, S.; Heims, F.; Pryjomska-Ray, I.; Haack, P.; Metzinger, R.; Bill, E.; Dau, H.; Comba, P.; Ray, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 1711−1715.
(222) Egan, J. W.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445−2446.
(223) Reinaud, O. M.; Theopold, K. H. *J. Am. Chem. Soc.* **1994**, *116*, 6979−6980.
(224) Eames, E. V.; Hernandez Sanchez, R.; Betley, T. A. *Inorg. Chem.* **2013**, *52*, 5006−5012.
(225) King, E. R.; Sazama, G. T.; Betley, T. A. *J. Am. Chem. Soc.* **2012**, *134*, 17858−17861.
(226) Semproni, S. P.; Hojilla Atienza, C. C.; Chirik, P. J. *Chem. Sci.* **2014**, *5*, 1956−1960.
(227) Obligacion, J. V.; Semproni, S. P.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 4133−4136.
(228) Tang, F. Z.; Zhang, Y.; Rath, N. P.; Mirica, L. M. *Organometallics* **2012**, *31*, 6690−6696.
(229) Vedernikov, A. N. *Acc. Chem. Res.* **2012**, *45*, 803−813.
(230) Prantner, J. D.; Kaminsky, W.; Goldberg, K. I. *Organometallics* **2014**, *33*, 3227−3230.
(231) Pal, S.; Zavalij, P. Y.; Vedernikov, A. N. *Chem. Commun.* **2014**, *50*, 5376−5378.
(232) Sberegaeva, A. V.; Liu, W.-G.; Nielsen, R. J.; Goddard, W. A.; Vedernikov, A. N. *J. Am. Chem. Soc.* **2014**, *136*, 4761−4768.
(233) Liu, W.-G.; Sberegaeva, A. V.; Nielsen, R. J.; Goddard, W. A.; Vedernikov, A. N. *J. Am. Chem. Soc.* **2014**, *136*, 2335−2341.

DOI: 10.1021/ic502515x
Inorg. Chem. 2015, 54, 5043−5052

(234) Petersen, A. R.; Taylor, R. A.; Vicente-Hernández, I.; Mallender, P. R.; Olley, H.; White, A. J. P.; Britovsek, G. J. P. *J. Am. Chem. Soc.* **2014**, *136*, 14089−14099.
(235) Taylor, R. A.; Law, D. J.; Sunley, G. J.; White, A. J. P.; Britovsek, G. J. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 5900−5903.
(236) Olah, G. A. *Acc. Chem. Res.* **1987**, *20*, 422−428.
(237) Periana, R. A.; Mirinov, O.; Taube, D. J.; Gamble, S. *Chem. Commun.* **2002**, 2376−2377.
(238) Jarosińska, M.; Lubkowski, K.; Sośnicki, J. G.; Michalkiewicz, B. *Catal. Lett.* **2008**, *126*, 407−412.
(239) Gang, X.; Zhu, Y. M.; Birch, H.; Hjuler, H. A.; Bjerrum, N. J. *Appl. Catal., A* **2004**, *261*, 91−98.
(240) Ding, K.; Metiu, H.; Stucky, G. D. *ACS Catal.* **2013**, *3*, 474−477.
(241) Buddrus, J.; Plettenberg, H. *Angew. Chem., Int. Ed.* **1976**, *15*, 436−436.
(242) Konnick, M. M.; Hashiguchi, B. G.; Devarajan, D.; Boaz, N. C.; Gunnoe, T. B.; Groves, J. T.; Gunsalus, N.; Ess, D. H.; Periana, R. A. *Angew. Chem., Int. Ed.* **2014**, *53*, 10490−10494.
(243) Fokin, A. A.; Schreiner, P. R. *Adv. Synth. Catal.* **2003**, *345*, 1035−1052.
(244) Olah, G. A.; Gupta, B.; Farina, M.; Felberg, J. D.; Ip, W. M.; Husain, A.; Karpeles, R.; Lammertsma, K.; Melhotra, A. K.; Trivedi, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 7097−7105.
(245) Fortman, G. C.; Boaz, N.; Munz, D.; Konnick, M. M.; Periana, R. A.; Groves, J.; Gunnoe, T. B. *J. Am. Chem. Soc.* **2014**, *136*, 8393−8401.
(246) Couto, A. B.; de Souza, D. C.; Sartori, E. R.; Jacob, P.; Klockow, D.; Neves, E. A. *Anal. Lett.* **2006**, *39*, 2763−2774.
(247) Kalman, S. E.; Munz, D.; Fortman, G. C.; Boaz, N. C.; Groves, J. T.; Gunnoe, T. B. *Dalton Trans.* **2015**, *44*, 5294−5298.

DOI: 10.1021/ic502515x
Inorg. Chem. 2015, 54, 5043−5052