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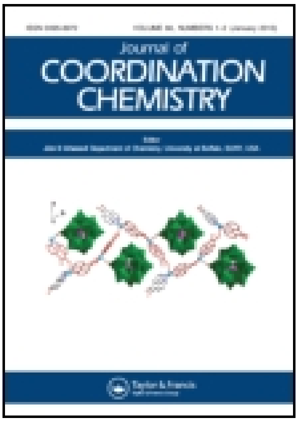

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

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Accepted author version posted online: 23 Apr 2013.Published online: 30 May 2013.

To cite this article: Akella Sivaramakrishna , Pothini Suman , E. Veerashekhar Goud , Sannapaneni Janardan , Chinduluri Sravani , Thota Sandeep , Kari Vijayakrishna & Hadley S. Clayton (2013) Review: active homogeneous reagents and catalysts in n-alkane activation, Journal of Coordination Chemistry, 66:12, 2091-2109, DOI: 10.1080/00958972.2013.797572

To link to this article: http://dx.doi.org/10.1080/00958972.2013.797572

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 12, 2091–2109, http://dx.doi.org/10.1080/00958972.2013.797572

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Review: active homogeneous reagents and catalysts in *n*-alkane activation reactions

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(*Received 24 June 2012; in final form 18 February 2013*)

The development of selective, efficient, and direct routes for activation and functionalization of naturally abundant *n*-alkanes could lead to a new paradigm in materials and energy technologies. In this context, the use of homogeneous catalysts to functionalize C–H bonds of unactivated hydrocarbons is of particular interest from a scientific as well as an economic viewpoint. Despite the large body of work on stoichiometric C–H activation reactions produced over the last three decades, relatively few systems have been developed to allow catalytic functionalization of hydrocarbons. This review deals with homogeneous catalytic processes available in the literature for paraffin activation and functionalization. The key intermediates involved in catalytic systems are highlighted, providing important information in the design of new and efficient catalysts. Also, some of the key challenges and approaches to rational development of the next generation of organometallic catalysts will be highlighted.

Keywords: Homogeneous; Catalysis; C–H activation; Metal–alkyl intermediate species; *n*-Alkanes

1. Introduction

Although there are major advances in the activation of hydrocarbons with a variety of reagents and routes, the development of effective and selective methods for homogeneous catalytic functionalization of inactive carbon–hydrogen bonds in saturated hydrocarbons still remains a major challenge [1–10]. Discussions on contrasting stabilities of branched alkanes conclude that the activation strongly depends on the interactions associated with various substituted patterns [11], including the hydrogen bonding properties of alkanes [12]. Oxidation reactions are most studied among the activation of *n*-alkanes [13–20]. While selective oxidations to alcohols are often limited by the use of stoichiometric metal-containing oxidants including $KMnO_4$ and CrO_3 [13–18], recently considerable research has been directed towards catalytic oxidation of alkanes in homogeneous solutions using late transition metals such as Pt(II) and Pd(II). The efficient and mild oxidation of alkanes

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Dedicated to (the late) Prof. F. Gordon A. Stone (1925–2011) into a mixture of alkyl hydroperoxides, alcohols, and ketones [3–10] which, can then be further transformed to more valuable products such as ketones and aldehydes [13–17], is of significant industrial importance. Attempts to fill the gaps between different approaches towards the selective activation and functionalization of *n*-alkanes have been well compared and documented [18]. The mechanistic understanding of C–H and C–C bond activation by metal complexes is well studied and has been reviewed elsewhere [19]. There are several significant factors that can influence the selective oxidation of paraffins pertaining to catalyst design, which were highlighted by Albonetti *et al.* [20]. The important reactions reported in the literature on functionalization of paraffins through various catalytic approaches are presented in figure 1 [21].

Even though there are many examples of C–H activation mediated by a wide range of metal complexes, the conversion of metal–alkyl intermediates into useful organic products is still a challenge. In addition, the manner in which the entire sequence of reactions can be made catalytic is also still unresolved. The development of new selective routes and catalytic systems for the oxidative functionalization of alkanes and other substrates using various transition metal complexes including copper(II) [3–6], [22–34] and a series of multi-metallic catalysts were reported [35–45]. Among them, hydrosoluble tetracopper(II) triethanolaminate complex is the most active and versatile Cu catalyst for (i) the oxygenation of alkanes by hydrogen peroxide [40–42], (ii) the hydrocarboxylation of alkanes with CO and H_2O to carboxylic acids [43, 44], and (iii) the aerobic oxidation of benzylic alcohols to aldehydes [45]. It has also been shown that the combination of a hydrosoluble tetracopper(II) complex with an oxidant such as tert-butyl hydroperoxide gives a versatile system for oxidative functionalization of various alkanes [46]. The current leading research efforts on activation of C–H bonds using homogeneous catalysts are principally focused [47–49] on organometallic chemistry. This route involves the formation of a bond between carbon and a metal center i.e. the C–H activation step. The scope of this section of review not only

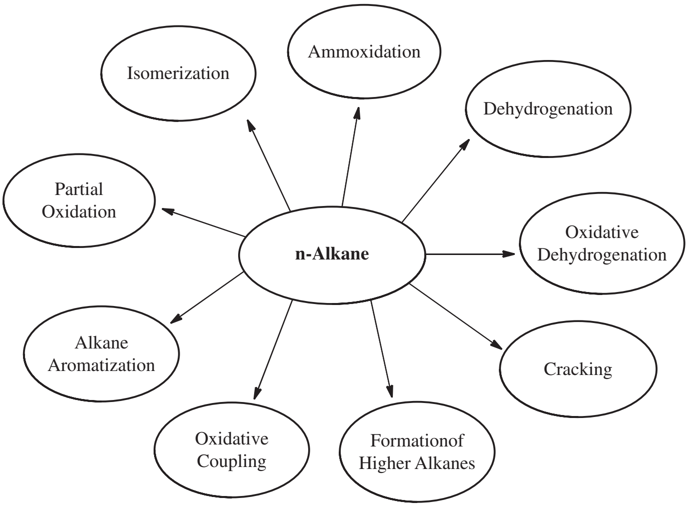


Figure 1. Possible C–H activation transformations of *n*-alkanes initiated by catalysts.

surveys the catalytic C–H activation reactions of *n*-alkanes, but also various metal–alkane complexes (or adducts) which are key intermediates in catalytic reactions.

2. Stoichiometric reagents to catalysts for C–H activation reactions

In general, hydrocarbon activation can proceed by five possible transformations: (i) the very well-known combustion reaction, (ii) the breaking of C–H bond by forming a direct C–X bond, where X can be any functional group, (iii) C–C coupling reactions that yield higher hydrocarbons, (iv) formation of M-alkane complexes as stable intermediates, and (v) by the formation of active intermediates through agostic interactions (figure 2). It is important to note that the mechanisms in each of the above steps may be different and dependent on reaction conditions.

The range of C–H bonds that can be activated by these metal complexes is large and also includes methane. Though there are many known metal and ligand systems that have taken a key role in C–H activation of paraffins, the platinum group metals, Pt [49, 50], Rh [51], Ir [52], Fe [53], Ru [54], and Os [55], have proved to be particularly useful in this regard. Other notable classes of C–H activators include (a) late transition-metal complexes, where C–H bonds are oxidatively added to the metal centers, (b) transition-metal, lanthanide, and actinide complexes that facilitate C–H activation via M-C σ-bond metathesis, and (c) early- to mid-transition-metal complexes that add C–H bonds across M = N and M = C linkages. The mechanism of C–H activation effected by metals was extensively studied and it is believed that paraffins give the corresponding alkene–hydride cations via a number of pathways including (i) alkane coordination to form a C–H σ complex, (ii) oxidative cleavage of the coordinated C–H bond to give a M- alkyl–methyl–hydride intermediate, (iii) reductive coupling to generate a methane σ complex, (iv) dissociation of methane, and (v) β–H elimination to form the desired products [56].

A notable contribution from Bergman and co-workers reported that iridium and rhodium complexes convert alkanes into hydridoalkyl–metal complexes (M + R–H → R–M–H) through formation of dihydrides, e.g. Cp × (L)IrH$_2$. Irradiation with ultraviolet light causes the dihydride complex to lose H$_2$, generating intermediates of the type Cp*ML (M = Ir or Rh). These coordinatively unsaturated intermediates react rapidly with C–H bonds affording the hydridoalkyl-metal complexes Cp*(L)M(R)(H) through oxidative insertion by

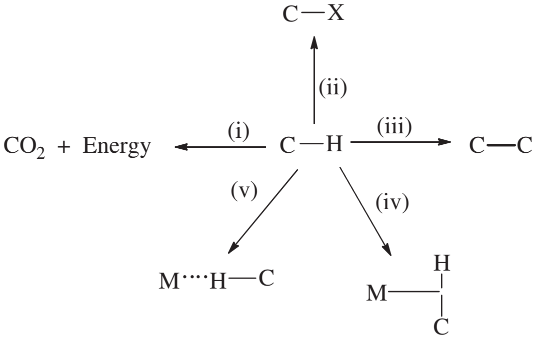


Figure 2. Different modes of C–H bond activation reactions.

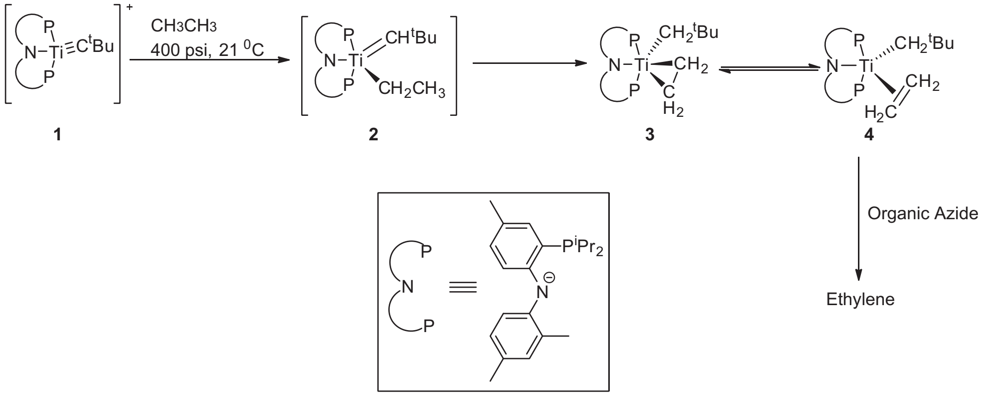
a simple three-center transition state. The reaction mechanism does not involve organic free radicals as intermediates [57]. Sodium acetate promoted C–H bond activation reactions using $[Cp^*MCl_2]_2$ (M = Ir, Rh) were reported and also substrates with electron-donating substituents react significantly faster than substrates with electron-withdrawing substituents, which is consistent with an electrophilic C–H activation mechanism [58].

Shilov and Shulpin discovered a remarkable alkane functionalization reaction that converts methane to methanol or methyl chloride under mild conditions [5]. As they outlined, the catalytic oxidation of alkanes follows different nontraditional mechanisms including activation by metal complexes via metal–alkyl intermediates with subsequent oxidation and the well-known radical chain mechanism [59]. These mechanisms are further supported by the research of Chen and Li where they studied the interaction of transition-metal ions (Cr^+, Mn^+, Fe^+, Co^+, Ni^+, Cu^+, and Ag^+) with long chain alkanes by mass spectroscopic methods [60].

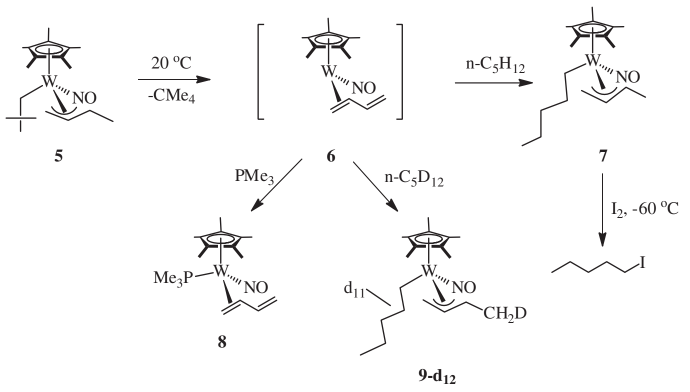
Shulpin and co-workers have demonstrated the oxidation reactions of alkanes by the system hydrogen peroxide–$[Mn_2L_2O_3][PF_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–carboxylic acid [61].

The titanium alkylidyne (**1**), (PNP)Ti≡C^tBu (PNP = *N*[2-PiPr2-4-methylphenyl]2^-), activates a C–H bond of ethane at room temperature, by transferring a *β*-hydrogen of the resulting ethyl ligand to the adjacent alkylidene ligand (**2**) and this forms an ethylene adduct of titanium (**3** and **4**). Treatment of the ethylene complex with organic azides yields ethene through formation of a mononuclear titanium-amido complex (scheme 1) [62]. Theoretical studies using computational methods have further investigated the role of alkanes in selective C–H activation [63]. These calculations indicate that a weak alkane C–H bond yields a more strongly bound adduct. Studies of various organometallic alkane complexes, which are key reactive intermediates, have been reviewed by Cowan, including the characterization of relatively stable complexes [64].

Rhenium-based organometallic-alkane complexes, $[Re(Cp)(CO)(PF_3)(alkane)]$ and $[Re(Cp)(CO)_2(alkane)]$ (alkane = cyclohexane, cyclopentane, pentane), have been prepared by photolysis of $[Re(Cp)(CO)_2(PF_3)]$ in the presence of corresponding alkane solvent. These complexes were identified and studied by NMR and IR spectroscopy [65].



Scheme 1.

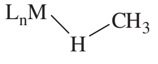


Scheme 2.

The tungsten allylnitrosyl complex, [Cp*W(NO)(η^3-CH$_2$:CHCHMe)(CH$_2$CMe$_3$)] (**5**, Cp*=η^5-C$_5$Me$_5$), selectively activates the terminal C–H bonds of pentane and heptane, affording the thermally stable alkyl tungsten compounds [Cp*W(NO)(η^3-CH$_2$:CHCHMe) [(CH$_2$)$_n$Me]] (**7**; $n = 4$, 6) (scheme 2). The *n*-pentyl group was selectively eliminated from **8** by treatment with I$_2$ and recovered as 1-iodopentane. In this sequence of reactions, C–H activation proceeds via two distinct steps, comprising the initial formation of the intermediate η^2-diene complex [Cp*W(NO)(η^2-CH$_2$:CHCH:CH$_2$)] (**7**) via β–H elimination of neopentane from **7**, and the subsequent formation of **9** through addition of pentane. Intermediate **7** can be trapped by PMe$_3$ as the [Cp*W(NO)(η^2-CH$_2$:CHCH:CH$_2$)(PMe$_3$)] adduct (**8**) [66].

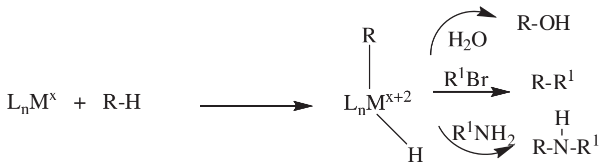
Most recent work in this area has largely been directed towards simple alkane complexation without C–H bond cleavage, stoichiometric alkane reactions, and catalytic alkane conversion. True alkane complexes of the type L$_n$M(HR) (**10**) are very rare as shown in equation (1). However, these complexes are known and were first detected [67] in an alkane matrix with agostic interactions at low temperature by UV/vis spectroscopy after the expulsion of CO from the hexacarbonyl precursor (equation (1)).

$$\mathrm{M(CO)_6} \xrightarrow{h\nu,\ \mathrm{Alkane}} \mathrm{M(CO)_5(alkane)} \quad (\mathrm{M = Mo}) \tag{1}$$



(10)

The fundamental reactions in activation of alkanes by various metal complexes in homogeneous solution were very well reviewed by Labinger and Bercaw [8]. Those include: *oxidative addition* of alkanes to low valent metal complexes (equation (2)), *sigma-bond metathesis*, where the reaction mainly occurs through the interchange of alkyl fragments (equation (3)) [49], *metalloradical activation* in which the hydrogen atom is abstracted from an alkane by the metal center (equation (4)), *1, 2 – addition* which involves the addition of an alkane to a metal–nonmetal double bond (equation (5)), and *electrophilic activation* which leads to direct functionalization of alkanes (equation (6)).



11 (2)

$$L_nM{-}R \quad + \quad R'{-}H \longrightarrow L_nM{-}R' \quad + \quad R{-}H \qquad (3)$$

$$L_nM{-}H \quad + \quad R{-}H \longrightarrow L_nM{-}R \quad + \quad H{-}H \qquad (4)$$

$$(R'NH)_2Zr{=}NR' \quad + \quad RH \longrightarrow \underset{\mathbf{12}}{(R'NH)_3Zr{-}H} \qquad (5)$$

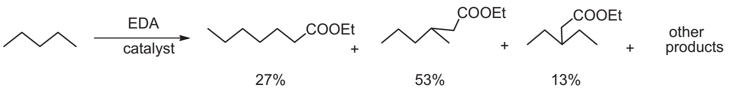
$$[por.Rh]_2 \xrightarrow{R-H} \underset{\mathbf{13}}{por.Rh{-}R} \; + \; por.Rh{-}H \qquad (6)$$

(por) = Porphyrin ligand

Transition metal C–H activations as well as C–C coupling reactions were studied [49] in detail to understand the mechanistic aspects of a variety of C–H activation reactions including those mediated by platinum complexes which were extensively reviewed by Tilset and Lersch [49].

C–H activation using copper complexes has been widely studied and well documented [24–34]; other group XI complexes are explored to less extent. However, silver(I) adducts containing highly fluorinated tris(pyrazolyl)borate, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$, were shown [68] as effective catalysts to catalyze carbene insertion into carbon–hydrogen bonds of cyclic and acyclic hydrocarbons at room temperature.

The complexes ($[Tp^{Br3}Ag]_2.CH_3COCH_3$) and $[Tp^{Br3}Ag(thf)]$ were shown [69] to functionalize several saturated linear and branched alkanes. The insertion of a carbene group from ethyl diazoacetate into the C–H bonds of alkanes was achieved with a conversion rate of nearly 25% attained for linear alkanes (equation (7)).

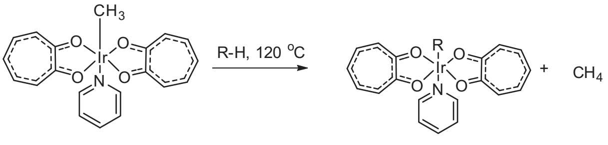


(7)

The activation of paraffins by a number of metallorganic compounds (particularly Fe-porphyrins), which act as selective oxidation catalysts was reported [70]. It was found [71] that the Fe-tetraphenylporphyrin compound oxidizes the isobutane solvent at 75 bar pressure and 80 °C to t-butanol with very high selectivity.

C–H activation of hydrocarbons to generate M–R intermediates at low temperatures with high yields and selectivities has been the focus [72] for a generation of “single-site” oxidation catalysts (equation (8)). Recently, Periana *et al.* have successfully demonstrated [73] C–H activation of various substrates using bis(tropolonato)Ir(III) complex (equation (9)).

$$\underset{\mathbf{14}}{L_nM_x^{+2}X_2} + R{-}H \longrightarrow L_nM_x + R{-}X + H{-}X \qquad (8)$$



15 **16** (9)

Hartwig and his team discovered a series of Cp*-rhodium boryl complexes produced by the photochemical reaction of [Cp*Rh(η^4-C_6Me_6)] with pinacolborane (HBpin) generating the bis-boryl complex [Cp*Rh(H)$_2$(Bpin)$_2$] (**17**), which reacts with neat HBpin to generate [Cp*Rh(H)(Bpin)$_3$] (**18**). Compounds **17** and **18** also react with alkanes and arenes to form alkyl- and aryl boronate esters at temperatures similar to or below those of the catalytic borylation of alkanes and arenes. Further, these compounds were observed directly in catalytic reactions. These results strongly suggest that the C–H bond cleavage process occurs by a metal-assisted σ-bond metathesis mechanism to generate a borane complex that isomerizes if necessary to place the alkyl group *cis* to the boryl group. This intermediate with *cis*-boryl and alkyl groups then undergoes B–C bond formation by a second σ-bond metathesis to generate the final functionalized product [74]. The regiospecific catalytic borylation of branched alkanes at the methyl group by ruthenium complexes and borane reagents to yield alkylboronates in good yields has also been reported [75, 76]. This selectivity occurs as the methyl group is sterically least hindered and most electron deficient.

Direct borylation via C–H bond activation of hydrocarbons catalyzed by Re, Ir, and Pd complexes was also reported [47]. There are some reports on stoichiometric borylation, which can be extended [77] to catalytic applications. An impressive catalyst system based on 5 mol% loading of [CpRh(C_2H_4)$_2$] and operating at 150 °C yielded 85% exclusively of (1-octyl)B(pinacolyl) from *n*-octane (see equation (10)).

$$\underset{\mathbf{19}}{R'_2B{-}BR'_2} + R{-}H \xrightleftharpoons{150\ ^\circ C} \underset{\mathbf{20}}{\underset{85\%}{R'_2B{-}R}} + R'_2B{-}H \qquad (10)$$

The selective borylation of sp^3 C–H bonds in alkanes in the presence of boranes catalyzed by Cp*Rh complexes was reported through formation of key intermediates in the catalysis reactions i.e. Cp*Rh(X)(Bpin) (X = H or Bpin), generated from Cp*Rh(H)$_2$(Bpin)$_2$ and Cp*Rh(H)$_2$(Bpin)$_3$ [74].

The catalytic oxidative addition to C–H bonds and electrophilic substitution [78] of C–H bonds of alkanes by highly reactive metal complexes is a very promising and constructive approach to convert alkanes (equation (11)) to their carboxylic acid [79], amine [80], and alcohol derivatives [81]. Short chain, gaseous alkanes such as methane, ethane, and propane were also carboxylated to give the corresponding acids [82].

$$CH_4 + CO \xrightarrow[\substack{K_2S_2O_8\,/\,TFA \\ 80\ ^\circ C,\ 20h}]{VO(acac)_2} \underset{93\%}{CH_3COOH} \qquad (11)$$

Catalytic oxidation of various hydrocarbons including alkanes with Cu(II)–Schiff base complex in the presence of hydrogen peroxide was evaluated for both homogeneous and heterogeneous systems, but the best results were obtained heterogeneously [83]. The transformation of alkanes was reported [84] on catalytic introduction of amino or hydroxyl groups to alkanes with C–N or C–O bond formation (equation (12)).

$$C_nH_{2n+2} \quad + \quad Me_3N \longrightarrow O \xrightarrow[150\ ^{o}C]{Cu(OAC)_2/\ TFA} \underset{15\%}{C_nH_{2n+1}CH_2NMe_2} \qquad (12)$$

Alkanes can be oxidized by H_2O_2 in acetonitrile using tetra-*n*-butylammonium salts of the vanadium-containing polyphosphomolybdate cluster $[PMo_{11}VO_{40}]_4^-$ as catalyst. These vanadium-containing heteropolyacids were very active in the transformation of methane to methyl trifluoroacetate along with a small amount of methyl acetate (equation (13)) [84]. The photochemical and photosynthetic functionalization of saturated hydrocarbons by α-dodecatungstophosphate in acetonitrile solution was reported (equation (14)) [85]. Significantly, there are no other reports on the observed photo activation of alkanes. However, oxidation reactions of various alkanes catalyzed by vanadate anion were reported using oligovanadates in the presence of H_2O_2 [86].

$$CH_4 \; + \; CO \xrightarrow[\substack{K_2S_2O_8/\ TFA/\ TFAA \\ 80\ ^{0}C,\ 20h}]{H_3PV_2Mo_{12}Mo_{40}} \underset{95\%}{CF_3COOCH_3} \; + \; CH3COOCH_3 \qquad (13)$$

$$RH\ (alkane) + h\nu \xrightarrow[CH_3CN,\ Pt(0)]{polyoxotungstate} \begin{array}{l} R\text{-}(2\ H)\ \ (alkene)\ \ +\ H_2 \\ RNHCO(CH_3)\ (N\text{-}alkylacetamide)\ + \\ RCO(CH_3)\ \ (alkyl\ methyl\ ketone) \end{array} \qquad (14)$$

Selective dehydrogenation of linear alkanes by pincer complexes was found to be an attractive alternative to the current commercial processes based on chromia-alumina catalysts. While many transition metal complexes are known to stoichiometrically add C–H bonds with terminal selectivity, PCP-pincer ligated iridium complexes (e.g. $(PCP)IrH_n$; $PCP = 2{,}6\text{-}C_6H_3(PR_2)_2$) have been shown to be the most effective catalysts to date for homogeneously catalyzed dehydrogenation of alkanes [87]. Recently, precursors of the phosphinite-ligated fragment (^{t}BuPOCOP)Ir were reported to be even more effective than (RPCP)Ir complexes for the benchmark cyclooctane/*t*-butylethylene transfer-dehydrogenation couple. But whereas (RPCP)Ir complexes (even for R groups less bulky than ^{t}Bu) show selectivity for *n*-alkanes (to give 1-alkenes) *versus* cyclooctane, the (^{t}BuPOCOP)Ir precursors give very high kinetic selectivity for cyclooctane. The selectivity between branched and *n*-alkanes has also been studied. It is found that (^{t}BuPCP)Ir catalysts show remarkably high selectivity (>1000 : 1) for dehydrogenation of a primary–secondary C–C linkage *versus* dehydrogenation of a primary–tertiary C–C linkage. The DFT calculations suggest that catalytic alkane dehydrogenation to alkene proceeds through (i) alkane oxidative addition, (ii) dihydride reductive elimination, (iii) *β*–H transfer from alkyl ligand to metal, and (iv) elimination of the olefin [87].

The first catalytic conversion of *n*-alkanes to alkylaromatics using “pincer”-ligated iridium complexes and olefinic hydrogen acceptors was reported by Brookhart and Goldman [88]. These authors report that the reaction of *n*-octane affords up to 86% yield of aromatic product, primarily o-xylene and secondarily ethylbenzene. In the case of *n*-decane and *n*-dodecane, the resulting alkylarenes are exclusively unbranched (i.e. *n*-alkyl-substituted), with selectivity for the corresponding o-(*n*-alkyl)toluene. In addition, recently Hartwig reported an unusual cyclization reaction, to form industrially important alkylarenes from alkanes, mediated by an iridium catalyst [89].

A series of $ReH_7(PPh_3)_2$ complexes were reported [90] for the stoichiometric dehydrogenation of linear alkanes to the corresponding dienes and their isomers. The addition of $P(OMe)_3$ led to the selective formation of 1-octene from *n*-octane in the presence of catalyst (equation (15)).

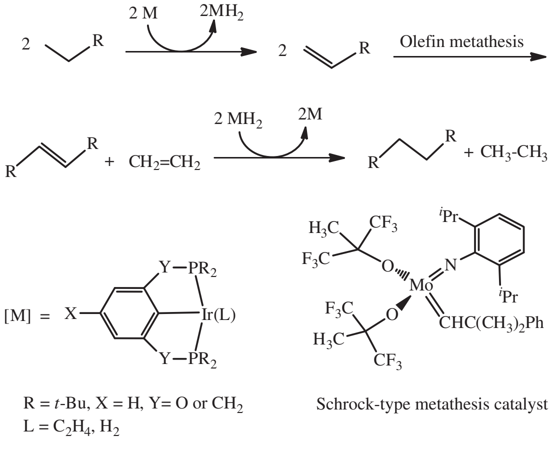
$$n\text{-octane} \xrightarrow[-H_2,\ 70^0C]{ReH_7(PPh_3)_2} \begin{array}{c}\text{A series of isomers}\\ \text{of octadiene}\end{array} \xrightarrow[ReH_7(PPh_3)_2]{P(OMe)_3,\ 60\ ^0C} \underset{98\%\ \text{selectivity}}{\text{1-octene only}} \tag{15}$$

$RhCl(CO)(PMe_3)_2$ causes the catalytic dehydrogenation of alkanes under irradiation to afford alkenes and dihydrogen without any H acceptor and with few secondary reactions [91]. The catalytic activity of $RhCl(CO)(PMe_3)_2$ is much superior to other metal phosphine carbonyl complexes (Fe, Ru, Co, Rh, Ir, Ni, and Pt). The catalysis conditions favor high temperature and low concentrations of the catalyst leading to high catalytic turnovers. The relative reactivities of alkanes (per C–H) in competitive dehydrogenation are: cyclooctane > cyclohexane > decane ≈ hexane. In order to get terminal alkenes from *n*-alkanes, high PMe_3/Rh ratios (5 : 1–10 : 1) were used. Irradiation is essential to initiate the reaction. The 14-electron $RhCl(PMe_3)_2$ intermediate, formed via CO dissociation, is suggested to be a possible active species for C–H activation.

Bergman used time-resolved infrared experiments to identify possible structures of all of the intermediates involved in C–H activation of $Tp^*Rh(CO)_2$ ($Tp^* = HB\text{-}Pz_3^*$, $Pz^* = 3,5$-dimethylpyrazolyl) in alkane solution [92].

A novel platinum-based catalyst, $LPt(II)(cyclo\text{-}C_6H_{10})H$, supported by a lipophilic dimethyl-di(4-tert-butyl-2-pyridyl)borate anionic ligand and *t*-butylethene as the sacrificial hydrogen acceptor has been used for dehydrogenation of alkanes [93].

A metathesis reaction was reported [94] with two catalytic systems with pincer ligands in which the metathesis of linear alkanes was achieved efficiently and selectively at moderate temperatures. The reaction proceeds via a tandem combination of two independent catalysts, one with activity for alkane dehydrogenation and the other for olefin metathesis (scheme 3).



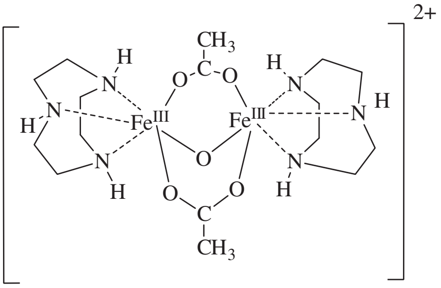
Scheme 3.

Another study with collision-induced dissociation mass spectroscopy supports the formation of bis(olefin)–metal ion complexes by dehydrogenation of linear alkanes ($>C_3$) with group VIII transition metal ions (Fe^+, Co^+ and Ni^+) via insertion into C–H bonds [95]. It is also observed that both Co^+ and Ni^+ are highly selective toward insertion into terminal C–C bonds, while Fe^+ shows considerably less selectivity.

Fujiwara and co-workers described the carboxylation, aminomethylation, and acetoxylation reactions of alkanes, which are catalyzed by highly electrophilic transition metal cationic species generated *in situ* in an acid medium through formation of alkyl-metal σ-complexes [96].

The development of catalysis using green oxidants, such as molecular oxygen or hydrogen peroxide, can offer an environmentally-friendly pathway for hydrocarbon oxidation. As the oxidants desirable for catalytic alkane conversion seem more compatible with coordination compounds than organometallic complexes, the coordination chemistry approach is currently attracting more attention [47]. The initial success in alkane oxidation via coordination compounds as catalysts was achieved [97] by Fenton. According to Fenton chemistry (also called Haber-Weiss chemistry), hydrogen peroxide and iron(II) salts can hydroxylate alkanes, but with poor yields. A dinuclear iron(III) complex has also been found to catalyze [53] the oxidation of alkanes with hydrogen peroxides in acetonitrile solution at room temperature; however, the reaction only proceeds in the presence of certain amino acids. The reaction scheme is shown in scheme 4. Later, other researchers attempted to oxidize the hydrocarbons with other iron complexes in the presence of molecular oxygen or hydrogen peroxide or even iodosylbenzene [98, 99].

The oxidation of alkanes by H_2O_2 [100] gives the corresponding alkyl hydroperoxides as the main products, which slowly decompose during the course of the reaction to produce the corresponding ketones (aldehydes) and alcohols depending on the reaction conditions. Recently, it was also found [101] that H_2O_2 oxidizes alkanes in acetonitrile at room temperature in the presence of a dinuclear iron complex with 1,4,7-triazacyclononane (TACN), compound **21**. Interestingly, this compound is also a model for bioinorganichemeythrins, found in O_2-transporting proteins.



21

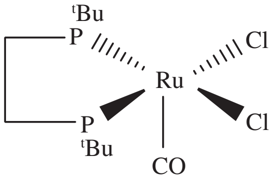
$$R\text{—}H + HO^{\cdot} \rightleftharpoons R^{\cdot} + H_2O$$

$$R^{\cdot} + O_2 \rightleftharpoons ROO^{\cdot}$$

$$ROO^{\cdot} + Fe^{II}\text{-}Fe^{II} \rightleftharpoons ROO^{-} + Fe^{III}\text{-}Fe^{II}$$

$$ROO^{-} + H^{+} \rightleftharpoons ROOH$$

Scheme 4.



28

Figure 3. Structure of carbonyl-(bis(di-*t*-butylphosphino)ethane-H,P,P′)-dichloro-ruthenium (**28**).

Germylenes Ge[CH(SiMe$_3$)$_2$]$_2$ (**22**) and Ge[N(SiMe$_3$)$_2$]$_2$ (**23**) react with alkanes (cyclohexane, cyclopentane, butane) in the presence of PhX (X = Cl, Br, I) to give R$_2$GeR$_1$X (**24**) (R = CH(SiMe$_3$)$_2$, N(SiMe$_3$)$_2$; R$_1$ = 2-tetrahydrofuranyl, 1,4-dioxan-2-yl, 1-ethoxyethyl, cyclopentyl, Cy (cyclohexyl), Bu, 1-methylpropyl). At high concentrations of the germylenes and iodobenzene the oxidative addition product R$_2$Ge(Ph)I (**25**) was obtained. High yields of C–H activation products can be obtained through high-dilution techniques. The regioselectivity of C–H activation was determined in reactions of **22** with butane and methylcyclopentane. The reaction rates were found to decrease in the order $CH > CH_2 > CH_3$, supporting suggestions of free radical participation in the activation step [102].

Rhodium carbenoids (dirhodiumtetrakis(S-(N-dodecylbenzenesulfonyl)prolinate) (Rh$_2$(S-DOSP)$_4$)) derived from methyl aryldiazoacetates can effectively catalyze asymmetric C–H activation of a range of alkanes and THF by a C–H insertion mechanism with good control of regioselectivity, diastereoselectivity, and enantioselectivity. Methyl-aryldiazoacetate-based carbenoids show better chemoselective than diazoacetates [103]. Davies *et al.* reported various rhodium-carbene complexes to activate C–H bonds and the reactivity of C–H bonds undergoing insertion shows the trend: methane > methylene > methyl. The selectivity strongly depends on steric factors [104].

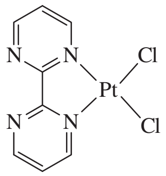
Mononuclear Ru(III) complexes [Ru(ntb)Cl$_2$]Cl (**26**) and [Ru(mntb)Cl$_2$]Cl (**27**) (ntb = tris(benzimidazol-2-ylmethyl)amine, mntb = tris(*N*-methylbenzimidazol-2-ylmethyl) amine) show catalytic activity of hydroxylation of alkanes in the presence of the peroxide TBHP and the peracid m-CPBA as cooxidants, illustrating that electronic and steric effects of tripodal 4N ligands can be tuned to catalyze the effective oxidative transformation of organic compounds [52]. In a similar way, compound **28** was reported by Pregosin *et al.* (figure 3) [105].

3. Catalytic and reversible C–H bond activation reactions

Even though a substantial number of metal complexes were involved in stoichiometric C–H bond activation reactions, very few of these have proven to be active catalysts. The Shilov catalysts are the most extensively studied [47] systems. These involve Pt(II) and related metals, usually in aqueous or other polar solvents. From a practical point of view, the problem with the Shilov system is that Pt(IV) is a very expensive oxidant (equation (16)). Periana's approach [106] has come closest to produce a practical system in the conversion of methane to methanol with the bipyrimidyl-Pt(II) complex **29** in concentrated H$_2$SO$_4$ at

220 °C. Methyl bisulfate (81%) was obtained after 90% of methane reacted with H_2SO_4.

$$CH_4 + PtCl_6^{2-} + H_2O \xrightarrow{120\ ^{\circ}C} CH_3OH + PtCl_4^{2-} + 2HCl \qquad (16)$$



29

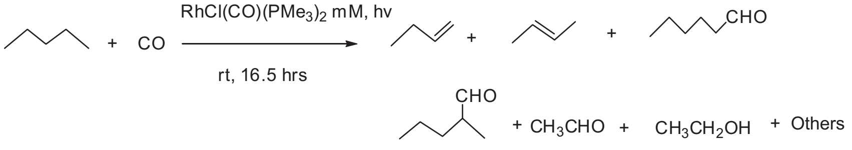
However, stoichiometric and catalytic photochemical borylation reactions have been investigated by Hartwig using [Cp′M(CO)$_3$] (Cp′ = C_5H_4Me, M = Mn; Cp′ = C_5H_5, M = Re; Cp′ = C_5Me_5, M = Re) (equation (17)) [107].

In a number of cases, alkane carbonylation was also reported [108] using [RhCl(CO)(PMe_3)$_2$] as catalyst on photolysis, which is the reverse of aldehyde decarbonylation.

$$R'_2B{-}BR'_2 + R{-}H \overset{h\nu}{\rightleftharpoons} R'_2B{-}R + R'_2B{-}H \qquad (17)$$

Dehydrogenation resulting from β-hydride elimination also proceeded as a side reaction to give 1- and 2-pentenes in the reactions of equations (18) and (19). The carbonylation of *n*-pentane yielded C_6-aldehydes, C_6-alcohols, butenes, acetaldehyde, and ethanol. The regioselectivity of the carbonylation was extremely high with selective formation of linear aldehyde (hexanal) obtained. A number of other interesting systems for the activation of alkanes in an acidic medium using a variety of oxidants such as MnO_4^-, IO_6^-, $S_2O_8^{2-}$, and Ce(IV) are also known [9].

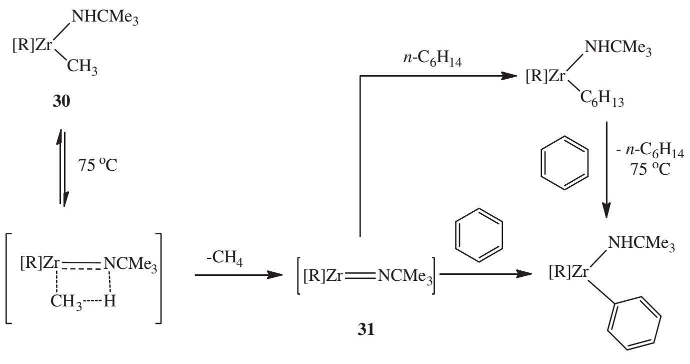
$$R{-}H + CO \longrightarrow RCHO \qquad (18)$$



(19)

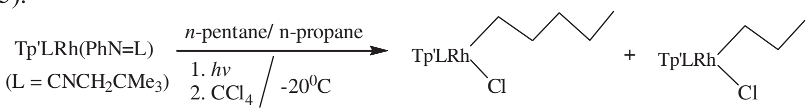
The coordinatively unsaturated 16-electron [Tp′RhL] reactive fragment (Tp′ = tris-(3,5-dimethylpyrazolyl)borate; L = $CNCH_2CMe_3$) activates hydrocarbons through formation of Rh-alkyl complexes of the type Tp′Rh(L)(R)(H). These complexes were converted to stable chlorides immediately following the activation of the bonds via photolysis of Tp′Rh(L)(PhN:C:NCH_2CMe_3) [109]. The coordinatively unsaturated 16-electron reactive Rh complex was used for activation of C–H bonds in linear, cyclic, and branched hydrocarbons, yielding the corresponding alkyl complexes, Tp′Rh(L)(R)(H), which were subsequently converted to the stable chlorides following activation of the bonds via photolysis (equation (20)) [109].

Bergman *et al.* reported [110] a metallocene system which cleanly and quantitatively activates a wide range of *n*-alkane, alkene, and arene C–H bonds. The pre-catalyst (methyl)(amido)zirconium (**30**) undergoes 1,2-methane elimination to form the transient



Scheme 5.

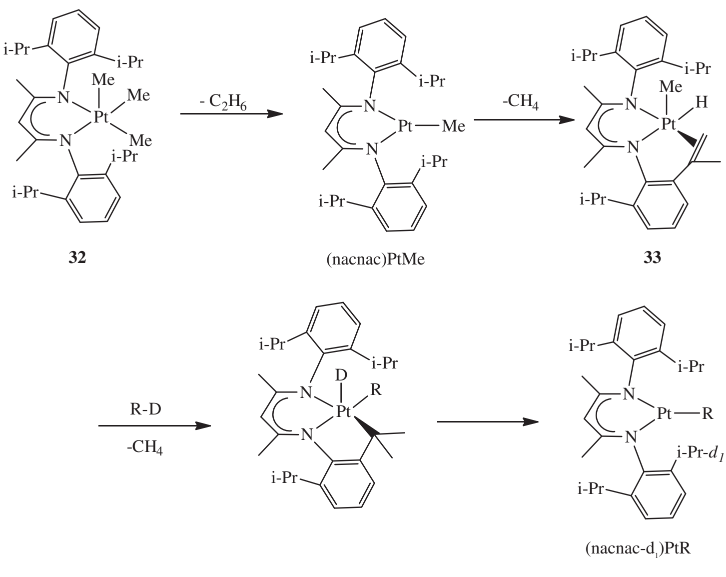
imido intermediate (**31**) followed by 1,2-C–H bond addition of a hydrocarbon substrate (scheme 5).



(20)

Goldberg *et al.* reported [111] a different approach using the five-coordinate platinum (IV)-alkyl complex (nacnac)PtMe$_3$(X) (**32**), (nacnac-) $[\{(o\text{-}^{i}\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{NC(CH_3)}\}_2\mathrm{CH}]^{-}$, X = H, R. In this complex, intramolecular C–H activation occurs through formation of a HPt(alkene) species (**33**) under mild conditions (scheme 6).

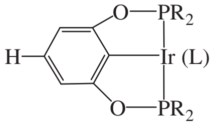
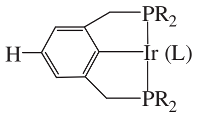
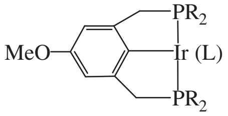
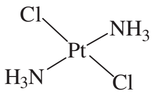
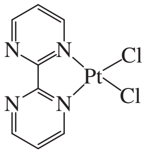
A scandium alkyl complex, Cp$^*_2$ScCH$_2$CMe$_3$, was synthesized [112] by addition of a pentane solution of LiCH$_2$CMe$_3$ to Cp$^*_2$ScCl at low temperature. This complex reacts with C–H bonds of hydrocarbons including methane and cyclopropane to yield corresponding



Scheme 6.

hydrocarbyl complex and CMe_4. Very recently, Periana *et al.* [46, 113] described several modern advances in designing catalysts for CH activation reactions and also the basic requirements for practical systems with emphasis on the issues that have prevented promising reported systems from becoming commercially viable.

Table 1. Some important homogeneous catalysts for C–H activation reactions.

Catalyst used	Experimental conditions	*n*-alkane used as substrate	Products formed	Selectivity	Turnover frequency or final conversion	Refs.
 **34.1**: R = ^{t}Bu; L = C_2H_4, H_2	Schrock-type catalyst, Re_2O_7/ Al_2O_3, 175 °C, 5 days	*n*-hexane (7.6 M)	Higher and lower *n*-alkanes	*n*-decane (721 mM)	2.81 M	[89]
 **34.2**: R = ^{t}Bu; L = H_4 and/ or H_2	Schrock-type catalyst, Re_2O_7/ Al_2O_3, 175 °C, 46 h	*n*-hexane (7.6 M)	Higher and lower *n*-alkanes	*n*-decane (399 mM)	1.81 M	[89]
 **34.3**: R = ^{i}Pr; L = H_4 and/ or H_2	Schrock-type catalyst, Re_2O_7/ Al_2O_3, 175 °C, 9 days	*n*-decane (5.1 M)	*n*-alkanes	Higher alkane (753 mM)	4.37 M	[89]
 **35**	Conc.H_2SO_4, 180 ° C, 15 min	Methane	Methyl bisulfate	>90%	10^{-3} sec	[101]
 **29**	102% H_2SO_4, 220 °C, 2.5 h	Methane	Methyl bisulfate	81%	90%	[101]
PdX_2, X= Halogen, **30**	96% H_2SO_4, 7 h	Methane	Methanol and CH_3COOH	89%	120 mM	[125]

Even though C–H bond activation to form C–N bonds was initiated in 1960 [114], Breslow and coworkers were able to demonstrate Mn(III) and Fe(III) porphyrins mediated nitrene insertion into C–H bonds [115]. Subsequently, $Rh_2(OAc)_4$ was used as a catalyst in high-yielding amination reactions [116]. Motherwell and coworkers reported a system containing iron chloride and chloramine-T formed a ferrous nitrene species that would selectively monoaminate tertiary C–H bonds through formation of oxenoid intermediate similar to P-450 oxidations [117]. Using a much different approach, Che and coworkers have developed a palladium catalyzed cascade C–H activation/nitrene insertion [118]. This methodology allows for functionalization of primary aliphatic C–H bonds in high yields.

Various metal catalyzed direct C–H amination reactions reported also produce stoichiometric amounts of by-products from the external oxidants [119] and other additives [120]. Other efficient amination reactions include Rh-catalyzed direct C–H amidation using sulfonyl azides as the amine source [121], which proceeds without external oxidants and releases only N_2. Some other elegant examples of catalytic C–H amination were reported using aryl or vinyl azides through intramolcular conversions [122, 123]. Du Bois and coworkers have described intramolecular Rh-catalyzed amination of C–H bonds by oxidative C–H insertion of sulfamate esters or carbamates to give six- or five-membered rings, respectively [124].

There are several other homogeneous methods for activation of paraffins including UV irradiation [125]. Esswein and Nocera elegantly reviewed the photocatalysis of various alkanes to produce hydrogen using mercury and other metal polypyridyl photosensitizers, transition metal complexes (Pt, Rh, Ru, and Ir), metal complexes of phosphines, porphyrins, terpyridine, homoleptic metal carbonyl complexes, redox shuttles, sacrificial donors, hydrogenases, and other reagents [126]. Methane can be converted into higher alkanes (from C_2 to C_6) continuously by UV (185 nm) irradiation in the presence of water vapor, which involves the coupling of alkyl radicals formed by hydrogen abstraction with OH radicals produced following UV irradiation of water [127].

4. Future developments and conclusions

Many organometallic complexes undergo reactions with alkanes, but unfortunately most of these systems are not amenable to catalytic transformations since the reactive organometallic species is extremely sensitive to stoichiometric oxidants. Nevertheless, this is an area of considerable research and the most efficient C–H activation procedures involving stoichiometric reactions are expected to be replaced by catalytic reactions, which are more advantageous economically. There is considerable commercial interest in this field as the industrially applicable process for selective oxidation of *n*-alkanes to give alcohols and carbonyl compounds is gaining a lot of significance in modern catalytic chemistry. Transition metal-mediated C–H bond activation reactions illustrate several efficient ways of functionalization, including the generation of metal carbenes which can activate the paraffins. The main challenge for organometallic approaches to this transformation remains to produce a stable and highly active catalyst. There will be a rapid growth in searching for new techniques and modifications to the existing methodologies for the functionalization of hydrocarbons as many research groups try to intensify their efforts. Some of the successful homogeneous catalysts for activation and functionalization of C–H bonds in paraffins are presented in table 1. It is very significant to note that a central consideration in the design of C–H activation based catalysts is the choice of ligands.

Acknowledgments

Dr ASRK is grateful to Council of Scientific and Industrial Research New Delhi (CSIR, INDIA) for the grant (Ref. No. 01(2541)/11/EMR-II). The authors are also thankful to VIT University for the support and facilities.

References

[1] K.I. Goldberg, A.S. Goldman (Eds.). Activation and Functionalization of C–H Bonds, ACS Symp. Ser. 885, American Chemical Society, Washington, DC (2004).
[2] G. Strukul (Ed.). *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer Academic, Dordrecht (1992).
[3] (a) A.E. Shilov, G.B. Shulpin. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer, Boston (2000); (b) S. Taubmann, C.M. Denner, H.G. Alt. *J. Organomet. Chem.*, **694**, 2005 (2009).
[4] (a) G.B. Shulpin. In *Transition Metals for Organic Synthesis*, M. Beller, C. Bolm (Eds.), Vol. 2, 2nd Edn, pp. 215–242, Wiley-VCH, Weinheim/New York (2004); (b) G.B. Shulpin. *Org. Biomol. Chem.*, **8**, 4217 (2010).
[5] A.E. Shilov, G.B. Shulpin. *Chem. Rev.*, **97**, 2879 (1997).
[6] G.B. Shulpin. *Mini-Rev. Org. Chem.*, **6**, 95 (2009).
[7] A.A. Fokin, P.R. Schreiner. *Chem. Rev.*, **102**, 1551 (2002).
[8] J.A. Labinger, J.E. Bercaw. *Nature*, **417**, 507 (2002).
[9] A. Sen. *Acc. Chem. Res.*, **31**, 550 (1998).
[10] R.H. Crabtree. *J. Organomet. Chem.*, **689**, 4083 (2004).
[11] (a) J.F. Gonthier, M.D. Wodrich, S.N. Steinmann, C. Corminboeuf. *Org. Lett.*, **12**, 3070 (2010); (b) A.M. Kirillov, M.V. Kirillova, A.J.L. Pombeiro. *Coord. Chem. Rev.*, **256**, 2741 (2012) and references therein.
[12] R. Cabot, C.A. Hunter, L.M. Varley. *Org. Biomol. Chem.*, **8**, 1455 (2010).
[13] G. Tojo, M. Fernandez. *Oxidation of Alcohols to Aldehydes and Ketones: A Guide to Current Common Practice*, Springer, New York (2006).
[14] I.W.C.E. Arends, R.A. Sheldon. In *Modern Oxidation Methods*, J.-E. Backvall (Ed.), pp. 83–118, Wiley-VCH, Weinheim (2004).
[15] R.A. Sheldon, I.W.C.E. Arends, G.-J. Ten Brink, A. Dijksman. *Acc. Chem. Res.*, **35**, 774 (2002).
[16] R.A. Sheldon, I.W.C.E. Arends, A. Dijksman. *Catal. Today*, **57**, 157 (2000).
[17] (a) M. Besson, P. Gallezot. *Catal. Today*, **57**, 127 (2000); (b) J. Muzart. *Tetrahedron*, **59**, 5789 (2003).
[18] A. Corma. *Catal. Rev. Sci. Eng.*, **46**, 369 (2004).
[19] S. Conejero, M. Paneque, M.L. Poveda, L.L. Santos, E. Carmona. *Acc. Chem. Res.*, **43**, 572 (2010).
[20] S. Albonetti, F. Cavani, F. Trifiro. *Catal. Rev. Sci. Eng.*, **38**, 413 (1996).
[21] A. Sivaramakrishna, P. Suman, E.V. Goud, S. Janardan, C. Sravani, C.S. Yadav, H.S. Clayton. *Res. Rev. Mater. Sci. Chem.*, **1**, 75 (2012).
[22] (a) G.B. Shulpin. *J. Mol. Catal.*, **189**, 39 (2002); (b) G.B. Shulpin. *C .R. Chimie*, **6**, 163 (2003).
[23] (a) T.C.O. MacLeod, M.V. Kirillova, A.J.L. Pombeiro, M.A. Schiavon, M.D. *Assis. Appl. Catal., A*, **372**, 191 (2010); (b) R.R. Fernandes, M.V. Kirillova, J.A.L. da Silva, J.J.R. Frausto da Silva, A.J.L. Pombeiro. *Appl. Catal., A*, **353**, 107 (2009).
[24] (a) M.V. Kirillova, M.L. Kuznetsov, P.M. Reis, J.A.L. da Silva, J.J.R. Frausto da Silva, A.J.L. Pombeiro. *J. Am. Chem. Soc.*, **129**, 10531 (2007); (b) M.V. Kirillova, A.M. Kirillov, P.M. Reis, J.A.L. da Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro. *J. Catal.*, **248**, 130 (2007).
[25] (a) A.M. Kirillov, M. Haukka, M.V. Kirillova, A.J.L. Pombeiro. *Adv. Synth. Catal.*, **347**, 1435 (2005); (b) M.N. Kopylovich, A.M. Kirillov, A.K. Baev, A.J.L. Pombeiro. *J. Mol. Catal. A: Chem.*, **206**, 163 (2003).
[26] (a) G.B. Shulpin, Y.N. Kozlov, L.S. Shulpina, A.R. Kudinov, D. Mandelli. *Inorg. Chem.*, **48**, 10480 (2009); (b) A.J. Bonon, D. Mandelli, O.A. Kholdeeva, M.V. Barmatova, Y.N. Kozlov, G.B. Shulpin. *Appl. Catal., A*, **365**, 96 (2009).
[27] (a) D. Mandelli, A.C.N. do Amaral, Y.N. Kozlov, L.S. Shulpina, A.J. Bonon, W.A. Carvalho, G.B. Shulpin. *Catal. Lett.*, **132**, 235 (2009); (b) M. Kirillov, M.V. Kirillova, L.S. Shulpina, P.J. Figiel, K.R. Gruenwald, M.F.C.G. da Silva, M. Haukka, A.J.L. Pombeiro, G.B. Shulpin. *J. Mol. Catal. A: Chem.*, **350**, 26 (2011).
[28] M.V. Kirillova, M.L. Kuznetsov, V.B. Romakh, L.S. Shulpina, J.J.R. Frausto da Silva, A.J.L. Pombeiro, G. B. Shulpin. *J. Catal.*, **267**, 140 (2009).
[29] L.S. Shulpina, M.V. Kirillova, A.J.L. Pombeiro, G.B. Shulpin. *Tetrahedron*, **65**, 2424 (2009).
[30] D. Mandelli, K.C. Chiacchio, Y.N. Kozlov, G.B. Shulpin. *Tetrahedron Lett.*, **49**, 6693 (2008).
[31] D. Mandelli, Y.N. Kozlov, C.C. Golfeto, G.B. Shulpin. *Catal. Lett.*, **118**, 22 (2007).
[32] V.B. Romakh, B. Therrien, G. Suss-Fink, G.B. Shulpin. *Inorg. Chem.*, **46**, 1315 (2007).

[33] Y.N. Kozlov, V.B. Romakh, A. Kitaygorodskiy, P. Buglyo, G. Suss-Fink, G.B. Shulpin. *J. Phys. Chem. A*, **111**, 7736 (2007).
[34] G.B. Shulpin, T. Sooknoi, V.B. Romakh, G. Suss-Fink, L.S. Shulpina. *Tetrahedron Lett.*, **47**, 3071 (2006).
[35] K.R. Gruenwald, A.M. Kirillov, M. Haukka, J. Sanchiz, A.J.L. Pombeiro. *Dalton Trans.*, 2109 (2009).
[36] M.V. Kirillova, A.M. Kirillov, M.F.C.G. da Silva, A.J.L. Pombeiro. *Eur. J. Inorg. Chem.*, 3423, (2008).
[37] Y.Y. Karabach, A.M. Kirillov, M. Haukka, M.N. Kopylovich, A.J.L. Pombeiro. *J. Inorg. Biochem.*, **102**, 1190 (2008).
[38] C. Di Nicola, Y.Y. Karabach, A.M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari, A.J.L. Pombeiro. *Inorg. Chem.*, **46**, 221 (2007).
[39] D.S. Nesterov, V.N. Kokozay, V.V. Dyakonenko, O.V. Shishkin, J. Jezierska, A. Ozarowski, A.M. Kirillov, M.N. Kopylovich, A.J.L. Pombeiro. *Chem. Commun.*, 4605 (2006).
[40] A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, M. Haukka, M.F.C.G. da Silva, A.J.L. Pombeiro. *Angew. Chem. Int. Ed.*, **44**, 4345 (2005).
[41] A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, E.Y. Karabach, M. Haukka, M.F.C.G. da Silva, A.J.L. Pombeiro. *Adv. Synth. Catal.*, **348**, 159 (2006).
[42] M.V. Kirillova, Y.N. Kozlov, L.S. Shulpina, O.Y. Lyakin, A.M. Kirillov, E.P. Talsi, A.J.L. Pombeiro, G.B. Shulpin. *J. Catal.*, **268**, 26 (2009).
[43] M.V. Kirillova, A.M. Kirillov, M.L. Kuznetsov, J.A.L. Silva, J.J.R. Frausto da Silva, A.J.L. Pombeiro. *Chem. Commun.*, 2353 (2009).
[44] M.V. Kirillova, A.M. Kirillov, A.J.L. Pombeiro. *Adv. Synth. Catal.*, **351**, 2936 (2009).
[45] P.J. Figiel, A.M. Kirillov, Y.Y. Karabach, M.N. Kopylovich, A.J.L. Pombeiro. *J. Mol. Catal. A: Chem.*, **305**, 178 (2009).
[46] M.V. Kirillova, A.M. Kirillov, D. Mandelli, W.A. Carvalho, A.J.L. Pombeiro, G.B. Shulpin. *J. Catal.*, **272**, 9 (2010).
[47] (a) J.A. Labinger, J.E. Bercaw. Nature, 414, 507 (2002); (b) J.A. Labinger. *J. Mol. Catal. A: Chem*., **220**, 27 (2004); (c) R.A. Periana, G. Bhalla, W.J. Tenn, K.J.H. Tomes, X.Y. Lin, O. Mironov, C.J. Jones, V.R. Ziatdinov. *J. Mol. Catal. A: Chem*., **220**, 7 (2004); (d) A.E. Shilov, A.A. Shreinman. *Coord. Chem. Rev.*, **24**, 97 (1977).
[48] (a) R.H. Crabtree. *J. Chem. Soc., Dalton Trans*., 2437 (2001); (b) A.E. Shilov, G.B. Shulpin. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer, Dordrecht (2000); (c) P. Legzdins, C.B. Pamplin. *ACS Symp. Ser*, **885**, 184 (2004); (d) T. Ishiyama, N. Miyaura. *J. Organomet. Chem*., **680**, 3 (2003); (e) M.Y. Sinev. *J. Catal*., **216**, 468 (2003); (f) J.J. Eisch, A.A. Adeosun, S. Dutta, P.O. Fregene. *Eur. J. Org. Chem*., 2657 (2005).
[49] (a) G. Dyker. *Angew. Chem. Int. Ed*., **38**, 1698 (1999); (b) M. Lersch, M. Tilset. *Chem. Rev.*, **105**, 2471 (2005); (c) G.R. Kotelnikov, S.M. Komarov, V.P. Bespalov, D. Sanfilippo, I. Miracca. *Stud. Surf. Sci. Catal*., **147**, 67 (2004); (d) T. Waku, J.A. Biscardi, E. Iglesia. *J. Catal*., **222**, 481 (2004); (e) J.H. Lunsford. *Catal. Today*, **63**, 165 (2000); (f) C. Jia, T. Kitamura, Y. Fujiwara. *Acc. Chem. Res*., **34**, 633 (2001); (g) S. S. Stahl, J.A. Labinger, J.E. Bercaw. *Angew. Chem. Int. Ed*., **37**, 2180 (1998).
[50] (a) M.J. Ingleson, M.F. Mahon, A.S. Weller. *Chem. Commun*., 2398 (2004); (b) P.N. Kuznetsov, L.I. Kuznetsova, V.P. Tverdokhlebov, A.L. Sannikov. Khimicheskaya Tekhnologiya (Moscow, Russian Federation), 7–14 (2005); (c) L.C. Liang, J.M. Lin, W.Y. Lee. *Chem. Commun*., 2462 (2005); (d) M. Marczewski, A. Migdal, H. Marczewska. *Phys. Chem. Chem. Phys*., **5**, 423 (2003); (e) A.F. Heyduk, T.G. Driver, J.A. Labinger, J.E. Bercaw. *J. Am. Chem. Soc*., **126**, 15034 (2004); (f) T.G. Driver, M.W. Day, J.A. Labinger, J.E. Bercaw. *Organometallics*, **24**, 3644 (2005); (g) M.W. Holtcamp, L.M. Henling, M.W. Day, J.A. Labinger, J.E. Bercaw. *Inorg. Chim. Acta*, **270**, 467 (1998).
[51] W. Cui, B.B. Wayland. *J. Am. Chem. Soc*., **126**, 8266 (2004); (b) D. Astruc. *Acc. Chem. Res*., **33**, 287 (2000); (c) C. Aissa, A. Furstner. *J. Am. Chem. Soc*., **129**, 14836 (2007).
[52] (a) Y.G. Lin, B.T. Koo. *Tetrahedron Lett*., **46**, 385 (2005); (b) H.M.L. Davies, T. Hansen, M.R. Churchill. *J. Am. Chem. Soc*., **122**, 3063 (2000); (c) M. Paneque, M.L. Poveda, L.L. Sartos, V. Salazar, E. Carmona. *Chem. Commun*., 1838 (2004).
[53] (a) H. Felkin, T.F. Khan, R.H. Smith, L. Yingrui. *Tetrahedron Lett*., **26**, 1999 (1985); (b) G.V. Nizova, B. Krebs, G.S. Fink, S. Schindler, L. Westerheide, L.G. Cuervo, G.B. Shulpin. *Tetrahedron*, **58**, 9231 (2002).
[54] T. Shima, H. Suzuki. *Organometallics*, **24**, 3939 (2005).
[55] (a) K. Matsubara, A. Inagaki, M. Tanaba, H. Suzuki. *J. Am. Chem. Soc*., **121**, 7421 (1999); (b) G.B. Shulpin, Y.N. Kozlov, L.S. Shulpina, P.V. Petrovskiy. *Appl. Organomet. Chem*., **24**, 464 (2010).
[56] G.S. Chen, J.A. Labinger, J.E. Bercaw. *Proc. Nat. Acad. Sci. (USA)*, **104**, 6915 (2007).
[57] (a) R.G. Bergman. *Science*, **223**, 902 (1984); (b) A.A. Bengali, B.A. Arndtsen, P.M. Burger, R.H. Schultz, B.H. Weiller, K.R. Kyle, C.B. Moore, R.C. Bergman. *Pure Appl. Chem*., **67**, 281 (1995).
[58] L. Li, W.W. Brennessel, W.D. Jones. *Organometallics*, **28**, 3492 (2009).
[59] A.E. Shilov. *Stud. Surf. Sci. Catal*., **66**, 11 (1991).
[60] R. Chen, L. Li. *J. Am. Soc. Mass Spectrom*., **12**, 367 (2001).

[61] (a) Y.N. Kozlov, L.S. Shulpina, T.V. Strelkova, G.B. Shulpin. *Russ. J. Phys. Chem. A*, **84**, 1502 (2010); (b) Y.N. Kozlov, G.V. Nizova, G.B. Shulpin. *J. Phys. Org. Chem.*, **21**, 119 (2008); (c) G.B. Shulpin, M.G. Matthes, V.B. Romakh, M.I.F. Barbosa, J.L.T. Aoyagi, D. Mandelli. *Tetrahedron*, **64**, 2143 (2008); (d) G.B. Shulpin, Y.N. Kozlov, S.N. Kholuiskaya, M.I. Plieva. *J. Mol. Catal. A: Chem.*, **299**, 77 (2009); (e) G.V. Nizova, G.B. Shulpin. *Tetrahedron*, **63**, 7997 (2007).

[62] V.N. Cavaliere, M.G. Crestani, B. Pinter, M. Pink, C.-H. Chen, M.-H. Baik, D.J. Mindiola. *J. Am. Chem. Soc.*, **133**, 10700 (2011).

[63] T.R. Cundari, T.R. Klinckman, P.T. Wolczanski. *J. Am. Chem. Soc.*, **124**, 1481 (2002).

[64] A.J. Cowan, M.W. George. *Coord. Chem. Rev.*, **252**, 2504 (2008).

[65] (a) G.E. Ball, C.M. Brookes, A.J. Cowan, T.A. Darwish, M.W. George, H.J. Kawanami, P. Portius, *J. Rourke. Proc. Natl. Acad. Sci. (USA),* **104**, 6927 (2007); (b) D.J. Lawes, S. Geftakis, G.E. Ball. *J. Am. Chem. Soc.*, **127**, 4134 (2005).

[66] J.Y.K. Tsang, M.S.A. Buschhaus, P. Legzdins. *J. Am. Chem. Soc.*, **129**, 5372 (2007).

[67] B. Eguillor, M.A. Esteruelas, M. Olivan, E. Onate. *Organometallics*, **23**, 6015 (2004).

[68] A.D. Sadow, T.D. Tilley. *J. Am. Chem. Soc.*, **127**, 643 (2005).

[69] C. Hall, R.N. Perutz. *Chem. Rev.*, **96**, 3125 (1996).

[70] J.E. Kyons, P.E. Ellis, V.A. Durante, R.K. Grasselli, A.W. Sleight (Eds.). *Structure-activity and Selectivity Relationships in Heterogeneous Catalysis*, Elsevier, Amsterdam (1991).

[71] P.E. Ellis, J.E. Lyons, H.K. Myers. European Patent EP 0 296 712 A2.

[72] B.A. Arndsen, R.G. Bergman, T.A. Mobley, T.H. Peterson. *Acc. Chem. Res.*, **28**, 154 (1995).

[73] (a) G. Bhalla, R.A. Periana. *Angew. Chem. Int. Ed.*, **44**, 1540 (2005); (b) W.J. Tenn III, K.J.H. Young, G. Bhalla, J. Oxgaard, W.A. Goddard III, R.A. Periana. *J. Am. Chem. Soc.*, **127**, 14172 (2005) and citations therein.

[74] J.F. Hartwig, K.S. Cook, M. Hapke, C.D. Incarvito, Y. Fan, C.E. Webster, M.B. Hall. *J. Am. Chem. Soc.*, **127**, 2538 (2005).

[75] (a) J.M. Murphy, J.D. Lawrence, K. Kawamura, C. Incarvito, J.F. Hartwig. *J. Am. Chem. Soc.*, **128**, 13684 (2006); (b) J.F. Hartwig, *ACS Symp. Ser.,* **885,** 136 (2004).

[76] (a) T. Ishiyama, N. Miyaura. *J. Organomet. Chem.*, **680**, 3 (2003); (b) K.M. Waltz, J.F. Hartwig. *J. Am. Chem. Soc.*, **122**, 11358 (2000).

[77] H. Chen, S. Schlecht, T.C. Semple, J.F. Hartwig. *Science*, **287**, 1995 (2000).

[78] M.W. Holtcamp, J.A. Labinger, J.E. Bercaw. *J. Am. Chem. Soc.*, **119**, 848 (1997).

[79] M. Asadullah, Y. Taniguchi, T. Kitamura, Y. Fujiwara. *Appl. Organomet. Chem.*, **12**, 277 (1998).

[80] Y. Taniguchi, T. Kitamura, Y. Fujiwara, S. Horie, K. Takaki. *Catal. Today*, **36**, 85 (1997).

[81] M. Lin, T. Hogan, A. Sen. *J. Am. Chem. Soc.*, **119**, 6048 (1997) and references therein.

[82] M. Asadullah, T. Kitamura, Y. Fujiwara. *Angew. Chem. Int. Ed.*, **39**, 2475 (2000).

[83] S.M. Islam, A.S. Roy, P.M.M. Mondal, S. Mondal, D. Hossain, S. Banerjee, S.C. Santra. *J. Mol. Catal. A: Chem.*, **336**, 106 (2011).

[84] (a) Y. Taniguchi, S. Horie, K. Takaki, Y. Fujiwara. *J. Organomet. Chem.*, **504**, 137 (1995); (b) D. Piao, K. Inoue, H. Shibasaki, Y. Taniguchi, T. Kitamura, Y. Fujiwara. *J. Organomet. Chem.*, **574**, 116 (1999); (c) D.M. Morales, R. Redon, C. Yung, C.M. Jensen. *Inorg. Chim. Acta*, **357**, 2953 (2004); (d) G. Suss-Fink, L. Gonzalez, G.B. Shulpin. *Appl. Catal., A*, **217**, 111 (2001).

[85] R.F. Renneke, C.L. Hill. *J. Am. Chem. Soc.*, **110**, 5461 (1988).

[86] (a) M.V. Kirillova, M.L. Kuznetsov, Y.N. Kozlov, L.S. Shulpina, A. Kitaygorodskiy, A.J.L. Pombeiro, G.B. Shulpin. *ACS Catal.*, **1**, 1511 (2011); (b) V.B. Romakh, G. Suss-Fink, G.B. Shulpin. *Petrol. Chem.*, **48**, 440 (2008).

[87] (a) S. Niu, M.B. Hall. *J. Am. Chem. Soc.*, **121**, 3992 (1999); (b) D. Baudry, M. Ephritikine, H. Felkin, J. Zakrzewski. *Tetrahedron Lett.*, **25**, 1283 (1984); (c) M.C. Haibach, S. Kundu, M. Brookhart, A.S. Goldman. *Acc. Chem. Res.*, **45**, 947 (2012); (d) J. Choi, A.H.R. MacArthur, M. Brookhart, A.S. Goldman. *Chem. Rev.*, **111**, 1761 (2011).

[88] R. Ahuja, B. Punji, M. Findlater, C. Supplee, W. Schinski, M. Brookhart, A.S. Goldman. *Nat. Chem.*, **3**, 167 (2011).

[89] J.F. Hartwig, *Nat. Chem.*, **3**, 99 (2011) and references therein.

[90] G.V. Nizova, B. Chaudret, X.D. He, G.B. Shulpin. *Bull. Russ. Acad. Sci.*, **41**, 1138 (1992).

[91] T. Sakakura, T. Sodeyama, M. Tanaka. *New J. Chem.*, **13**, 737 (1989).

[92] S.E. Bromberg, H. Yang, M.C. Asplund, T. Lian, B.K. McNamara, K.T. Kotz, J.S. Yeston, M.F.H. Wilkens, R.G. Bergman. *Science*, **278**, 260 (1997).

[93] E. Khaskin, D.L. Lew, S. Pal, A.N. Vedernikov. *Chem. Commun.*, 6270 (2009).

[94] A.S. Goldman, A.H. Roy, Z. Huang, R. Ahuja, W. Schinski, M. Brookhart. *Science*, **312**, 257 (2006).

[95] D.B. Jacobson, B.S. Freiser. *J. Am. Chem. Soc.*, **105**, 5197 (1983).

[96] C. Jia, T. Kitamura, Y. Fujiwara. *Acc. Chem. Res.*, **34**, 633 (2001) and references therein.

[97] H.S.H. Fenton. *J. Chem. Soc., Trans.*, 899 (1894).

[98] (a) F.G. Doro, J.R.L. Smith, A.G. Ferreira, M.D. Assis. *J. Mol. Catal. A: Chem*., **164**, 97 (2000); (b) L. Smith, R. John, Y. Iamamoto, F.S. Vinhado. *J. Mol. Catal. A: Chem*., **252**, 23 (2006); (c) F.S. Vinhado, M.E.F. Gandini, Y. Iamamoto, A.M.G. Silva, M.M.Q. Smoes, M.G.P.M.S. Neves, A.C. Tome, S.L.H. Rebelo, A.M.V.M. Periana, J.A.S. Cavaleiro. *J. Mol. Catal. A: Chem*., **239**, 138 (2005).

[99] (a) T. Nagataki, Y. Tachi, S. Itoh. *J. Mol. Catal. A: Chem*., **225**, 103 (2005); (b) C.B. Woitiski, Y.N. Kozlov, D. Mandelli, G.V. Nizova, U. Schuchardt, G.B. Shulpin. *J. Mol. Catal. A: Chem*., **222**, 103 (2004); (c) A. Kumar, G.S. Mishra, A. Kumar. *J. Mol. Catal. A: Chem*., **201**, 179 (2003); (d) G.B. Shulpin, E.R. Lachter. *J. Mol. Catal. A: Chem*., **197**, 65 (2003).

[100] (a) R. Hage, A. Lienke. *J. Mol. Catal. A: Chem*., **251**, 150 (2006); (b) K.A. Miller, J.M. Bartolin, R.M. ONeill, R.D. Sweeder, T.M. Owens, J.W. Kampf, M.M.B. Holl, N.J. Wells. *J. Am. Chem. Soc*., **125**, 8986 (2003).

[101] K. Visvaganesan, E. Suresh, M. Palaniandavar. *Dalton Trans*., 3814 (2009).

[102] (a) G.B. Shulpin, A.R. Kudinov, L.S. Shulpina, E.A. Petrovskaya. *J. Organomet. Chem*., **691**, 837 (2006); (b) D.F.C. Guedes, T.C.O. MacLeod, M.C.A.F. Gotardo, M.A. Schiavon, I.V.P. Yoshida, K.J. Ciuffi, M.D. *Assis. Appl. Catal., A*, **296**, 120 (2005); (c) G.B. Shulpin, G.V. Nizova, Y.N. Kozlov, V.S. Arutyunov, A.C. M. Dos Santos, A.C.T. Ferreira, D. Mandelli. *J. Organomet. Chem*., **690**, 4498 (2005).

[103] (a) V.L. Lobachev, E.S.L. Rudakov. *Kinet. Catal*., **46**, 344 (2005); (b) L.P. Stepovik, M.V. Gulenova, I.M. Martynova. *Russ. J. Gen. Chem*., **75**, 507 (2005); (c) G.B. Shulpin, C.C. Golfeto, G. Suess-Fink, L.S. Shulpina, D. Mandelli. *Tetrahedron Lett*., **46**, 4563 (2005).

[104] (a) H.M.L. Davies. *Chem. Rev*., **103**, 2861 (2003); (b) H.M.L. Davies. *J. Org. Chem*., **74**, 6555 (2009); (c) H.M.L. Davies. *J. Am. Chem. Soc*., **126**, 10862 (2004); (c) H.M.L. Davies. *J. Am. Chem. Soc*., **128**, 1060 (2006); (d) H.M.L. Davies. *Nature*, **451**, 417 (2008).

[105] J.M. Goicoechea, M.F. Mahon, M.K. Whittlesey, P.G.A. Kumar, P.S. Pregosin. *Dalton Trans*., 588 (2005).

[106] R.A. Periana, D.J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii. *Science*, **280**, 560 (1998).

[107] H. Chen, J.F. Hartwig. *Angew. Chem., Int. Ed*., **38**, 3391 (1999).

[108] T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada, M. Tanaka. *J. Am. Chem. Soc*., **112**, 7221 (1990).

[109] (a) H.M. Hoyt, F.E. Michael, R.G. Bergman. *J. Am. Chem. Soc*., **126**, 1018 (2004); (b) A.J. Vetter, C. Flaschenriem, W.D. Jones. *J. Am. Chem. Soc*., **127**, 12315 (2005).

[110] U. Fekl, K.I. Goldberg. *J. Am. Chem. Soc*., **124**, 6804 (2002).

[111] H.V.R. Dias, R.G. Browning, S.A. Richey, C.J. Lovely. *Organometallics*, **23**, 1200 (2004).

[112] B.L. Conley, W.J. Tenn, III, K.J.H. Young, S.K. Ganesh, S.K. Meier, V.R. Ziatdinov, O. Mirinov, J. Oxgaard, J. Gonzales, W.A. Goddard, III, R.A. Periana. *J. Mol. Catal. A: Chem*., **251**, 8 (2006).

[113] (a) G.B. Shulpin, G.V. Nizova, Yu. V. Geletii. *J. Gen. Chem. USSR*, **57**, 548 (1987); (b) M.Y. Sinev. *Res. Chem. Intermed*., **32**, 205 (2006); (c) M.C. Asplund, P.T. Snee, J.S. Yeston, M.J. Wilkens, C.K. Payne, H. Yang, K.T. Kotz, H. Frei, R.G. Bergman, C.B. Harris. *J. Am. Chem. Soc*., **124**, 10605 (2002).

[114] M.F. Sloan, W.B. Renfrow, D.S. Breslow. *Tetrahedron Lett*., **5**, 2905 (1964).

[115] R. Breslow, S.L. Gellman. *J. Chem. Soc., Chem. Commun*., 1400 (1982).

[116] R. Breslow, S.L. Gellman. *J. Am. Chem. Soc*., **105**, 6728 (1983).

[117] D.H.R. Barton, R.S.H. Motherwell, W.B. Motherwell. *J. Chem. Soc., Perkin Trans*., **1**, 445 (1983).

[118] H.Y. Thu, W.Y. Yu, C.M. Che. *J. Am. Chem. Soc*., **128**, 9048 (2006).

[119] J. Ryu, K. Shin, S.H. Park, J.Y. Kim, S. Chang. *Angew. Chem. Int. Ed*., **51**, 1 (2012).

[120] A. Armstrong, J.C. Collins. *Angew. Chem. Int. Ed*., **49**, 2282 (2010).

[121] J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius. *Chem. Soc. Rev*., **40**, 4740 (2011).

[122] S.H. Cho, J.Y. Kim, J. Kwak, S. Chang. *Chem. Soc. Rev*., **40**, 5068 (2011).

[123] H.M.L. Davies, J. Du Bois, J.-Q. Chem. *Soc. Rev*., **40**, 1855 (2011).

[124] (a) C. Espino, P. Wehn, J. Chow, J. Du Bois. *J. Am. Chem. Soc*., **123**, 6935 (2001); (b) P. Wehn, J. Lee, J. Du Bois. *Org. Lett*., **5**, 4823 (2003).

[125] A.J. Esswein, D.G. Nocera. *Chem. Rev*., **107**, 4022 (2007).

[126] J.P. Oh, T. Matsumoto, J. Nakamura. *Catal. Lett*., **124**, 215 (2008).

[127] R.A. Periana, O. Mironov, D. Taube, G. Bhalla, C.J. Jones. *Science*, **301**, 814 (2003).