Homogeneous Catalysis

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Electrophilic Activation of Alkenes by Platinum(II): So Much More Than a Slow Version of Palladium(II)

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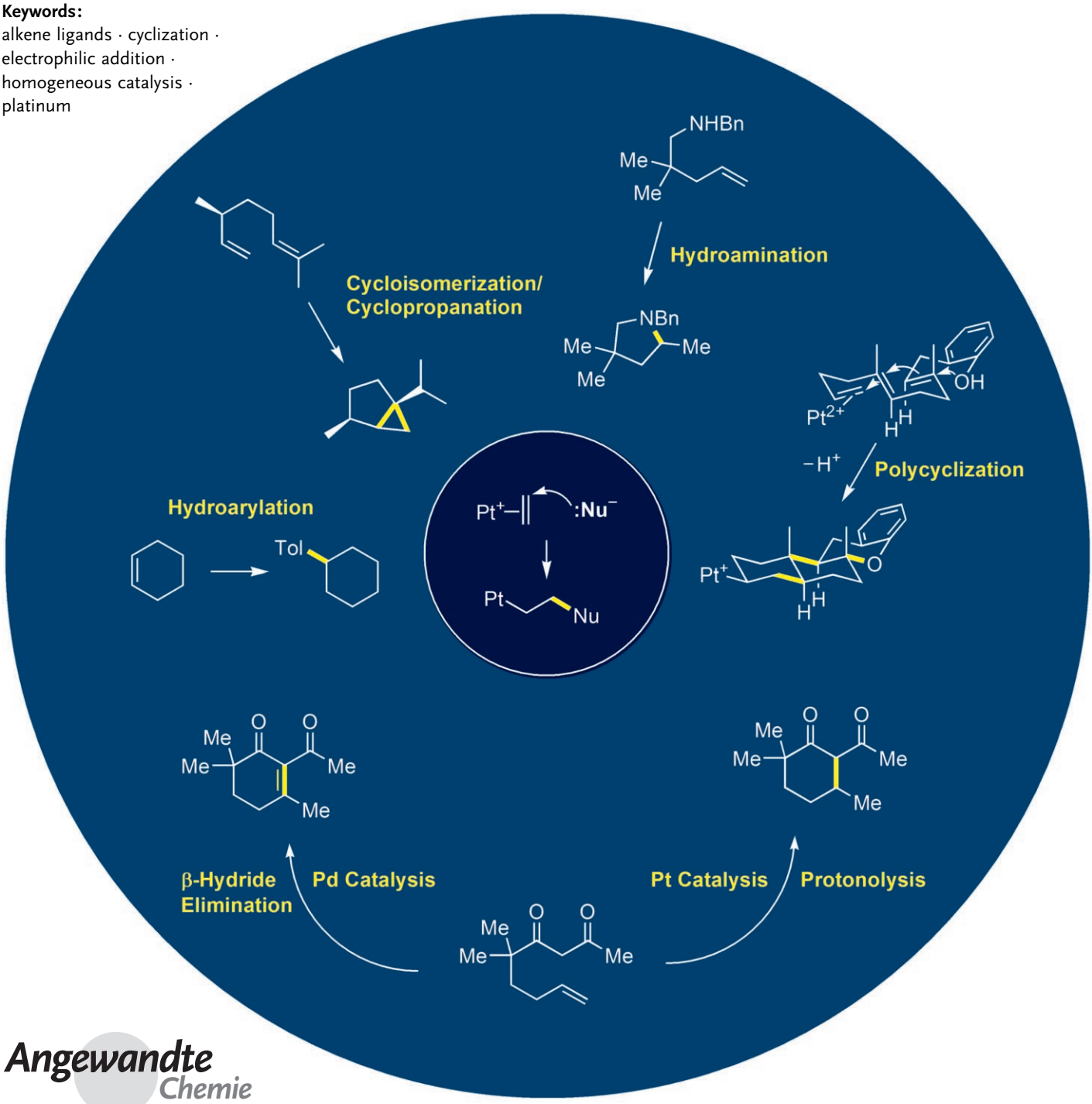

The electrophilic activation of alkenes by transition-metal catalysts is a fundamental step in a rapidly growing number of catalytic processes. Although palladium is the best known metal for this purpose, the special properties of its third-row cousin platinum (strong metal–ligand bonds and slow substitution kinetics) have enabled the development of transformations that are initiated by addition to the C=C bonds by protic carbon, nitrogen, oxygen, and phosphorus nucleophiles, as well as alkene or arene nucleophiles. Additionally, reactivity profiles, which are often unique to platinum, provide wholly new reaction products. This Review concerns platinum-catalyzed electrophilic alkene activation reactions, with a special emphasis on the mechanistic properties of known systems, on the differences between platinum and palladium catalysts, and on the prospects for the development of new systems.

From the Contents

1. Introduction

The electrophilic activation of an alkene on coordination to an electron-deficient metal ion is fundamental to organometallic chemistry, both conceptually and in synthetic applications. The Wacker process for the conversion of ethylene into acetaldehyde, a classic example of an efficient catalytic oxidation, begins with the coordination of ethylene to Pd^{II}, which activates the ethylene moiety toward nucleophilic attack by water. The development[1,2] of the Wacker process was a major driving force behind a huge amount of research performed in the 1960s and 1970s that was aimed at understanding the mechanistic details of nucleophilic attack on metal-coordinated olefins, especially in the platinum group. The key step is the reaction of a metal–olefin complex with a nucleophile to give a β-substituted metal–alkyl species. This transformation can in principle proceed through an inner-sphere or an outer-sphere mechanism, with opposite stereochemical outcomes, and with different implications for catalyst design. Mechanistic studies, both experimental and theoretical, have demonstrated that either pathway in fact can be operative, often under only subtly different conditions.

The integration of this reaction into a productive catalytic cycle requires the eventual cleavage of the newly generated M–C bond, and is often preceded by intermediate rearrangements or additions. In the last decade many diverse applications of this alkene activation have been discovered, which most commonly employ palladium(II) and platinum(II) catalysts. Both metals are quite efficient in the promotion of nucleophilic addition to a complexed olefin, but their distinct properties often lead to complementary modes of M–C bond cleavage. Specifically, as palladium complexes are reactive toward ligand substitution, M–C bond cleavage pathways that require substitution for the release of product, such as β-hydride elimination, are common (for example, the Wacker process). In contrast, platinum complexes are relatively inert toward ligand substitution. This facilitates the development of catalytic processes that involve alternative pathways for M–C bond cleavage, such as protonolysis, cation rearrangements, and cyclopropanation, and reduces the problems caused by competing olefin-isomerization reactions.

This review covers platinum-catalyzed reactions that involve the electrophilic activation of a C=C bond toward attack by a nucleophile, including protic oxygen, nitrogen, and carbon nucleophiles, arenes, and C=C bonds. When deemed appropriate, the related palladium-catalyzed processes are discussed. Stoichiometric examples of platinum-mediated olefin activation have been recently reviewed,[3] and only selected examples are discussed here. Related chemistry based on the platinum-catalyzed activation of alkynes, such as enyne cycloisomerization,[4–6] is not covered. Addition reactions that are commonly believed to proceed by a 1,2-migratory insertion of the olefin into a platinum–element bond, such as hydrogenation and hydrosilylation,[7] are also not covered.

2. Mechanistic Aspects and Theoretical Studies

The majority of catalytic reactions that involve the Pt-mediated activation of alkenes produce the net addition of an element–hydrogen bond (C–H, N–H, or O–H) across a C=C bond. With a few exceptions (see below), two potential mechanisms are most commonly considered. Scheme 1 depicts the generally preferred mechanism for Pt-catalyzed additions to alkenes.[8] Coordination of a C=C bond to an

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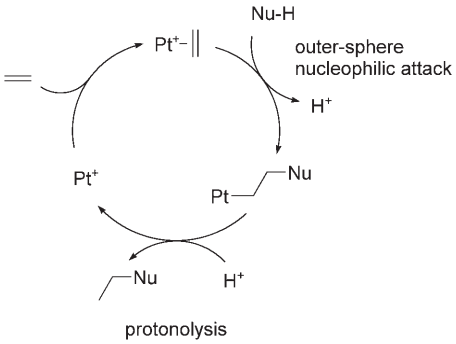
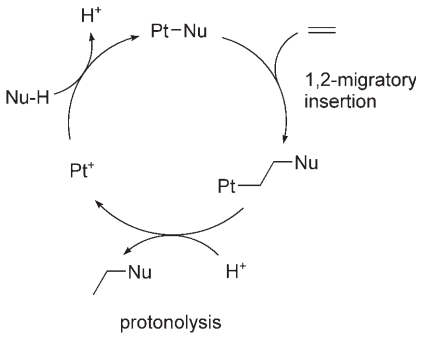


Scheme 1. Catalytic addition of NuH to an alkene by outer-sphere nucleophilic attack and protonolysis of the M–C bond.

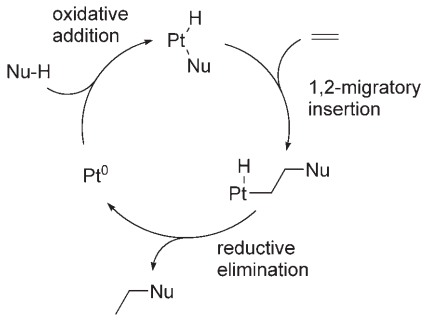
electrophilic Pt center activates the alkene toward outer sphere attack by a protic nucleophile NuH. The newly formed Pt–C bond is then cleaved by protonolysis (see below) to regenerate the catalyst.

Scheme 2 shows an alternate inner-sphere mechanism, in which the nucleophile first coordinates to Pt by deprotonation of NuH and ligand exchange. The key step is 1,2-migratory insertion of a bound olefin into the Pt–Nu bond. Again, the newly formed Pt–C bond is cleaved by protonolysis.



Scheme 2. Catalytic addition of NuH to an alkene by metalation, insertion, and protonolysis.

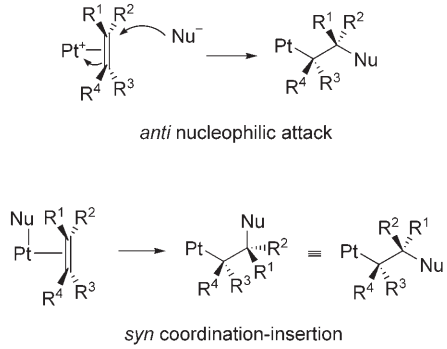
A variation on the inner-sphere mechanism, involving a Pt^{II}–Pt^{0} redox couple, is also possible (Scheme 3). Here, initial oxidative addition of NuH to Pt^{0} is followed by olefin insertion into the Pt–Nu bond. The resulting Pt–C bond is cleaved by a C–H reductive elimination rather than by



Scheme 3. Catalytic addition of NuH to an alkene by oxidative addition, insertion, and reductive elimination.

protonolysis. While this mechanism is generally preferred for more electron-rich metals such as rhodium and iridium, and is almost exclusively invoked for transition-metal-catalyzed olefin hydrogenation and hydrosilylation (not discussed here), several lines of evidence, discussed below, suggest that platinum-catalyzed additions of protic C–H, N–H, or O–H nucleophiles more likely proceed by the outer-sphere electrophilic activation mechanism shown in Scheme 1.

Importantly, these mechanisms are often distinguishable by stereochemical studies: the outer-sphere mechanism of Scheme 1 gives *anti* addition across the C=C bond, while the inner-sphere coordination/insertion mechanisms in Scheme 2 and 3 give *syn* addition (Scheme 4). Throughout this review, the proposed reaction mechanisms will be referred to as outer sphere, representing Scheme 1, or inner sphere, representing Scheme 2.



Scheme 4. Comparison of the stereochemical pathways for an outer-sphere nucleophilic attack (top) and an inner-sphere coordination/insertion (bottom).

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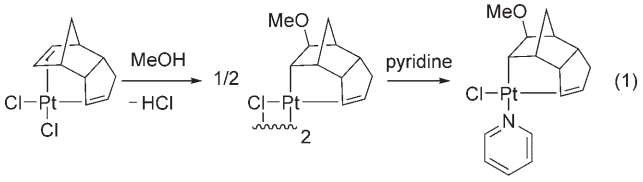
This section describes studies aimed at understanding the mechanisms of platinum-catalyzed alkene-activation reactions. Attention is focused first on theoretical and experimental studies relating to the Pt–C bond-forming step, nucleophilic attack on a π-coordinated Pt–olefin complex. Next, studies concerning the Pt–C bond-cleaving step, which usually proceeds by protonolysis, is discussed.

2.1. Nucleophilic Attack on Metal-Coordinated Alkenes: Experiments

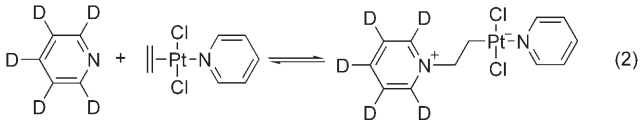
In 1908, Hofmann and von Narbutt[9] reported the reaction of K_2PtCl_4, dicyclopentadiene, and methanol to give adducts with loss of HCl. Although the structures could not be conclusively identified at the time, it was suggested that a C–OMe bond, rather than a Pt–OMe bond, had been formed. Through reactivity studies, Chatt et al.[10] demonstrated almost 50 years later that the products were chloride-bridged dimers, and analysis by derivatization supported the original proposal that the methoxy group was associated not with Pt as a methoxide ligand, but with the organic dicyclopentadiene fragment. The research group of Stille[11,12] determined by NMR the structure of the monomeric pyridine adduct, which results from the *exo* attack of methanol at the more strained double bond to give the β-methoxy Pt–alkyl shown [Eq. (1)]. This structure was later



(1)

confirmed by X-ray analysis.[13] Platinum(II) and palladium(II) complexes of chelating dienes were shown to react similarly with various nucleophiles, including acetate,[14] β-diketones,[15] amines,[14,16] and phosphines.[17]

Although platinum complexes of chelating dienes have been shown rather conclusively to undergo addition of nucleophiles by outer-sphere attack rather than inner-sphere coordination and insertion, the extension of this conclusion to systems with monoalkene ligands is tenuous. As chelated diene complexes are conformationally restricted, the olefin moieties are prevented from achieving the coplanar relationship necessary for insertion into a *cis* Pt–X bond.[18] Numerous examples of the addition of nucleophiles to Pt-complexed monodentate olefins have been demonstrated, but the stereochemistry of addition has not often been explored. Orchin and co-workers showed that pyridine adds reversibly to a neutral Pt–ethylene complex to give a zwitterionic σ-alkyl moiety [Eq. (2)].[19] The reaction was proven to be stereospecific by using *cis*-1,2-dideuterioethylene; no *cis*/*trans* isomerization accompanied the reversible addition.[20] A key observation from an elegant demonstration by Panunzi et al.[21] was that diethylamine adds to a diastereomerically resolved platinum complex of the prochiral olefin 1-butene to give, after protonolysis, only (*S*)-*N*,*N*′-diethyl-*sec*-butylamine, the product of Markovnikov addition with *anti* stereochemistry [Eq. (3)].



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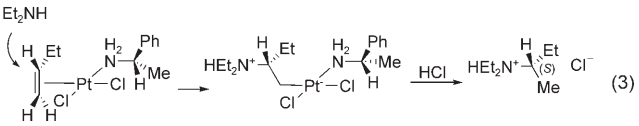
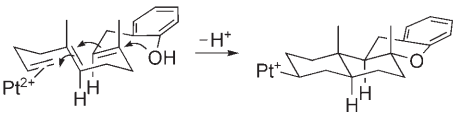


(3)

Stereochemical evidence for Markovnikov addition is also provided by the Pt-mediated tricyclization of a 1,5,9-trienylphenol to give a tetracyclic Pt–alkyl species with *trans* ring fusions.[22] In the proposed mechanism, attack of a trisubstituted olefin on a Pt-coordinated terminal olefin initiates a cation/olefin cascade that terminates with quenching by the phenol oxygen atom [Eq. (4)]. It is uncertain whether the reaction is fully concerted, or if discrete carbocationic

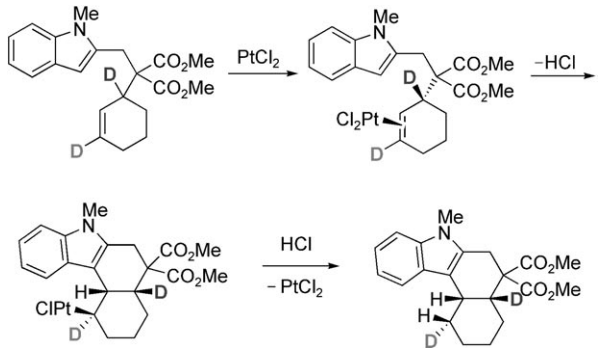


(4)

intermediates are formed, but the *trans* ring fusions in the product rule out an insertion cascade mechanism that begins with either *syn* or *anti* oxypalladation of a trisubstituted olefin.

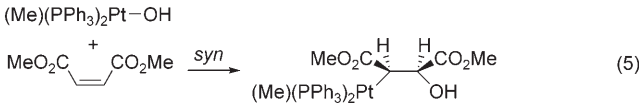
In a catalytic system, Widenhoefer and co-workers[23] have demonstrated that the intramolecular addition of indoles to alkenes (see Section 3.7) proceeds by nucleophilic attack of the indole on a Pt-coordinated alkene, rather than indole C–H bond activation followed by olefin insertion (outer-sphere mechanism). The cyclization of a deuterium-labeled substrate gave the expected stereoisomer for *anti* carboplatination followed by Pt–C bond protonolysis with retention of stereochemistry (Scheme 5). Notably, the related palladium-catalyzed oxidative cyclizations described by Ferreira and Stoltz proceed by C–H bond activation and insertion.[24]

Michel Gagné was born in 1965 in Canada. He obtained his BSc from the University of Alberta in 1987, his PhD from Northwestern in 1991, working with Professor Tobin J. Marks, and after postdoctoral stints with Professor Robert H. Grubbs and Professor David A. Evans as NSERC of Canada Fellow, took up his position at the University of North Carolina at Chapel Hill, where he is a Professor. His interests are broadly centered on catalysis, primarily at the interface of inorganic and organic chemistry.



Scheme 5. Outer-sphere nucleophilic attack of indole on a Pt-coordinated olefin (deuterium labeled) in a catalytic intramolecular hydroarylation process.

In a stoichiometric reaction designed to model the palladium-catalyzed hydration of maleate esters, dimethyl maleate was shown to react with *cis*-[Pt(OH)(Me)(PPh_3)$_2$] to give the *erythro*-β-hydroxyalkyl platinum complex, whose structure was verified by X-ray analysis [Eq. (5)].[25,26] The



(5)

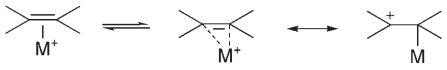
product configuration is consistent with *syn* migratory insertion of the alkene into the Pt–OH bond. As less-electrophilic olefins did not react in this manner, the mechanistic implications for other platinum-catalyzed additions to alkenes are uncertain.

Relevant studies that concerned nucleophilic additions to ethylene were directed at understanding the mechanism of the Wacker process,[1,2] in which a $PdCl_2$/$CuCl_2$ catalytic system promotes the conversion of ethylene into acetaldehyde, in which water is used as a nucleophile and dioxygen as a terminal oxidant. Initially, kinetic studies[27] seemed to indicate that the reaction proceeded by the 1,2-migratory insertion of a coordinated olefin into a Pd–OH bond to give a β-hydroxyalkyl, which after β-elimination and rearrangement would give the product. Evidence against this hypothesis was provide by stereochemical studies of model stoichiometric reactions that involved hydroxypalladation by Bäckvall et al.,[28,29] and Stille and Divakaruni.[30,31] The studies in fact suggested that an outer-sphere attack of water on a Pd-coordinated olefin was the key step. However, the debate has not been fully settled as kinetic and stereochemical evidence indicates that a different mechanism may operate in the model systems (high chloride concentration) compared to the actual Wacker process (low chloride concentration).[32–35]

Palladium-catalyzed intramolecular additions to unactivated alkenes have recently been explored in many contexts. In some cases, stereochemical evidence has been provided for *syn* addition[24,36–43] and in others, for *anti* addition.[37,39,44,45] Although a detailed discussion of these observations is outside the scope of this review, it is important to note that for palladium-catalyzed additions of carbon, nitrogen, and oxygen nucleophiles to C=C bonds, both *syn* and *anti* addition mechanisms appear possible, and the catalytic conditions determine which pathway is preferred. For platinum catalysis one might expect outer-sphere attack to be kinetically favored over the coordination/insertion pathway because of the much slower rates of ligand substitution for platinum relative to palladium.[46] Although the stereochemical evidence for platinum-catalyzed reactions to *unactivated* alkenes has thus far favored *anti* addition by outer-sphere nucleophilic attack on a coordinated olefin, it is not unreasonable to expect that *syn* addition by coordination/insertion can also occur.

2.2. Nucleophilic Attack on Metal-Coordinated Alkenes: Theory

Nucleophilic attack on a π-complexed olefin must involve a lowest unoccupied molecular orbital (LUMO) localized at the alkene (which resembles the π* orbital of the free olefin). However, Eisenstein and Hoffmann[47,48] pointed out that metals capable of π backbonding such as Pt^{II} should actually raise the energy of this LUMO, as the vacant π* orbital interacts with a filled d orbital of the metal of appropriate symmetry. With the help of extended Hückel calculations, it was predicted that the metal-bound olefin must in fact slip into η^1 coordination as in Scheme 6 to give a structure that



Scheme 6. The transition of a metal-coordinated alkene from η^2 to η^1 coordination ("slippage") facilitates the nucleophilic attack on the distal carbon.

may be drawn as a β-carbocationic platinum alkyl species (slippage signifies the transition from η^2 to η^1 coordination). The LUMO is now localized at the β carbon atom, and an increased overlap with the highest occupied molecular orbital (HOMO) of the nucleophile is predicted. Subsequent INDO (intermediate neglect of differential overlap) studies by Baird and co-workers[49] predicted that a π* orbital of an olefin should in fact be stabilized on complexation to a cationic iron fragment, even in the absence of slipping. However, slipping of the olefin caused a further decrease in the orbital energy.

In Pt-catalyzed additions to unsymmetrical alkenes, the nucleophile generally adds to the more highly substituted carbon atom (Markovnikov regioselectivity, see Section 3). This probably is a reflection of several factors, which include the preferred generation of a less sterically hindered metal–alkyl species, and the favored buildup of positive charge at the more highly substituted carbon atom (Scheme 6). Although regioselectivity is ultimately determined from the relative transition state energies, a distinct asymmetry of coordination is also present in the ground state. In the optimized geometry for propene coordinated to a dicationic platinum-pincer complex,[50] the terminal CH_2 group is found to be 0.15 Å closer to the metal center than the internal CHMe group (Figure 1).

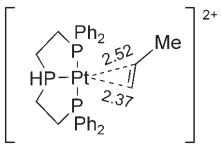
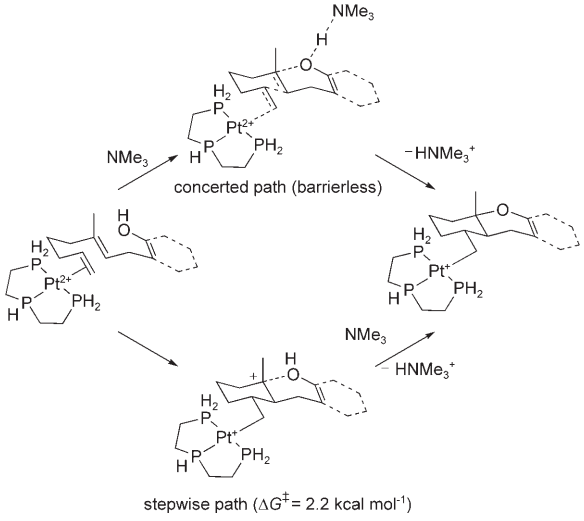


Figure 1. Asymmetric coordination of propene to a dicationic platinum center (from DFT calculations).

Recently, Senn et al.[51] reported a DFT study of the full catalytic cycle of the hydroamination of ethylene with ammonia, catalyzed by Group 9 and 10 metal complexes. For cationic Group 10 complexes, the mechanism is predicted to involve the outer-sphere nucleophilic attack of ammonia on the complexed ethylene. Dynamic reaction-path calculations indicate that the olefin slips from η^2 to η^1 coordination, concomitant with the approach of ammonia to the olefin. An analogous reaction path could not be found for neutral Group 9 complexes. A similar deformation was predicted by Sakaki et al. for attack of ammonia on a Pd–ethylene complex[52] using ab initio methods. Here, the use of cationic complexes allowed nucleophilic addition at coordinated ethylene, while the reaction was unfavorable for neutral and anionic complexes. Based on inductive principles, it is generally expected that an increase in the positive charge on a metal complex will increase the reactivity of coordinated olefins toward nucleophilic attack. This effect has been extensively documented and is the subject of a recent review.[3]

The platinum-mediated bicyclization of 1,6-dienylphenols [see Section 3.8, Eq. (37)] was recently characterized by DFT calculations.[50] The proposed mechanism[22] for this class of reaction, in which outer-sphere attack of a trisubstituted olefin on a Pt-coordinated terminal olefin is followed by quenching of the carbocation by a protic nucleophile, is supported by reaction-path calculations. A question that has not yet been addressed by experimental studies is whether this reaction proceeds in a stepwise or concerted fashion, that is, whether discrete carbocationic intermediates are involved (Scheme 7). A stepwise pathway, which involves the generation of the donor-stabilized cation shown, was located with a free-energy barrier at room temperature of only 2.2 kcal mol^{-1} starting from the Pt–alkene complex shown in Scheme 7. However, relaxed scanning along the reaction coordinate with a nearby amine base revealed a direct barrierless pathway for the transformation, which indicates that the transformation probably is concerted in the presence of base. In either pathway, addition occurs with *anti* stereochemistry to both the Pt-coordinated terminal alkene and the nucleophilic internal alkene.

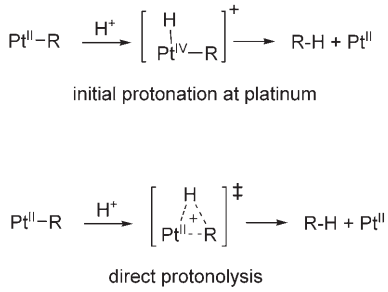


Scheme 7. Concerted and stepwise paths for the Pt-mediated bicyclization of a 1,6-dienylphenol.

In the design of catalysts that operate by the activation of alkenes toward nucleophilic attack, it is important to consider that enhancement of the electrophilicity of the metal complex will favor this step. However, many potential catalytic processes require that the newly formed metal–alkyl complex will react with an electrophile (for example, H^+ in protonolysis) to cleave the M–C bond and regenerate the catalyst. The reactivity in this step will *decrease* with an increase in the electrophilicity of the catalyst, so a balance must be achieved.

2.3. Protonolysis and Other Catalytically Relevant Pt–C Bond-Cleaving Reactions

Platinum–carbon bond protonolysis and its reverse, C–H activation by a platinum complex, have been well studied in the context of alkane oxidation catalysis, for example, the Shilov system. Mechanistic studies have indicated that the forward reaction may proceed by two processes: 1) initial protonation of a Pt^{II}–alkyl to give a Pt^{IV}–alkyl hydride species followed by C–H reductive coupling, or 2) direct protonation at the Pt–C bond to release alkane directly without oxidization of the platinum center (Scheme 8). As Pt–C bond protonolysis has recently been extensively reviewed,[53] only a limited discussion is presented here.

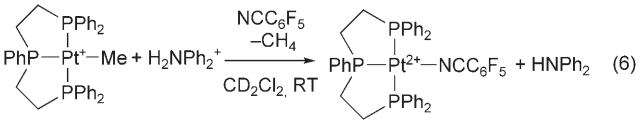


Scheme 8. Oxidative and non-oxidative modes for the protonolysis of the Pt–C bond.

The majority of the platinum-catalyzed alkene activation reactions discussed below almost certainly proceed by the initial generation of a Pt–alkyl complex followed by M–C bond protonolysis (for example, Scheme 1), and result in the net addition of NuH across the C=C bond. As is the case for many catalytic cycles, conditions that favor one step can disfavor the other. Although more electrophilic platinum–olefin complexes will favor the addition of a nucleophile to the olefin to give a β-substituted metal–alkyl complex (see above), protonolysis of the resulting M–C bond will be decreasingly favorable. The necessary balance has been

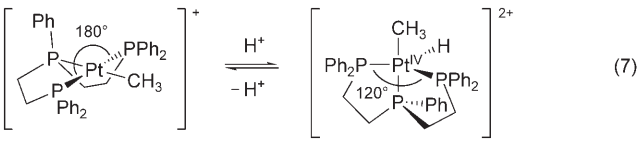
achieved in many cases (see below), but some electron-deficient metal–alkyl complexes are resistant to protonolysis, which may prevent the completion of a potentially useful catalytic cycle [see Eq. (37), Section 3.8].

One promising way to enhance the favorability of an associative process without significantly altering the electron density at the metal is to employ a ligand that geometrically favors the formation of the unstable intermediate. In studies of the protonolysis of cationic platinum–methyl complexes, it was observed that the pincer ligand triphos uniquely promotes Pt–C bond protonolysis to give methane, using a moderately strong diphenylammonium acid [$pK_a = 0.8$; Eq. (6)].[54] Combinations of mono- and bidentate ligands



(6)

failed to promote protonolysis unless the much stronger triflic acid was used. The current hypothesis is that triphos imparts a torsional strain on the starting square-planar Pt^{II} complex that is relieved on protonation to give a five-coordinate Pt^{IV} complex, which then reductively eliminates methane [Eq. (7)]. As nonpincer ligands lack this torsional strain, protonation at the metal is less favorable.



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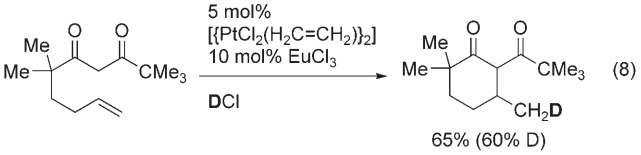
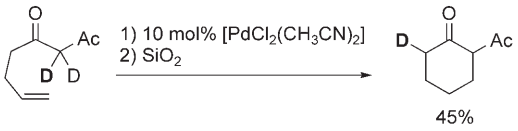
A large difference between the platinum- and palladium-catalyzed activation of olefins is the increased tendency of palladium to promote β-hydride elimination in intermediate metal–alkyl complexes, as will be demonstrated in the following sections. The result is that many palladium-catalyzed transformations give oxidized products, while the analogous platinum-catalyzed reactions are more prone to turnover by nonoxidative means, such as M–C bond protonolysis. This contrast is well illustrated in the intramolecular addition of β-diketone nucleophiles to unactivated olefins (see Section 3.6 for more details). A $PtCl_2/EuCl_3/HCl$ system catalyzes the 6-*exo*-cyclization of 4-pentenyl β-dicarbonyl compounds by an outer-sphere mechanism; the use of DCl gives the product shown in Equation (8) that results from the



(8)

direct protonolysis of the initially formed Pt–C bond.[55] In contrast, a cyclization of 3-butenyl β-dicarbonyl compounds catalyzed by $PdCl_2$ gives the product shown in Equation (9).[56] This result, along with other deuterium-labeling



(9)

experiments, indicates that the initially formed Pd–alkyl species undergoes several reversible β-hydride eliminations and reinsertions to give a Pd–enolate complex, which finally releases the product by protonolysis. Although both catalytic transformations eventually give a product by protonolysis, β-elimination and reinsertion are clearly much faster than the protonolysis of the Pd–alkyl species in the Pd system.

In addition to protonolysis, the Pt–C bond in principle can be cleaved in a myriad of ways to provide access to variously functionalized products. Catalytic turnover by β-hydride elimination is feasible, as long as the "Pt–H" generated can be efficiently oxidized (see Section 3.3). Palladium-catalyzed reactions are much more advanced in this respect, partly as a result of the highly developed technology for the reoxidization of Pd^0 to Pd^{II} using molecular oxygen,[57] in addition to benzoquinone and $CuCl_2$. Other modes of turnover, generally observed when no protic nucleophile is present in the system, involve the intermediate generation of carbocations, which are quenched by hydride or alkyl shifts [for example, Eq. (10)] to release product and regenerate the catalyst (see Section 3.8).

(10)

3. Catalysis

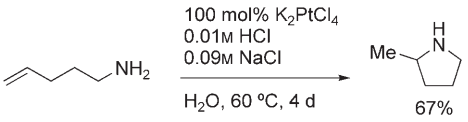
The stoichiometric addition of nucleophiles to metal-complexed olefins was extensively explored in the 1960s and 1970s, and efficient catalytic processes involving olefin activation by transition metals have been known since the 1950s. Despite this, the majority of progress in platinum-catalyzed alkene activation has occurred in the last ten years and includes the development of mild conditions (usually operating below 100 °C) for the addition of heteroatom (N, O, P) and carbon nucleophiles to activated and unactivated olefins. In some cases, platinum complexes promote reactivity that is complementary to analogous palladium-catalyzed reactions.

3.1. Nitrogen Nucleophiles: Platinum-Catalyzed Hydroamination of Alkenes

Catalytic hydroamination, the addition of an N–H bond across a multiple bond, is one of the most widely pursued transformations in organometallic chemistry.[58,59] Efficient

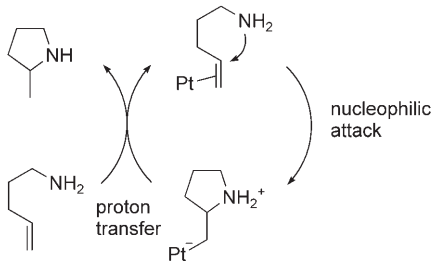
and mechanistically diverse catalysts for the hydroamination of alkenes and alkynes include Brønsted acids,[60,61] basic alkali-metal salts,[62] early transition metals,[63] lanthanides,[64] and late transition metals.[65,66] Although alkene hydroamination catalyzed by platinum was first demonstrated over 30 years ago, much of the development in this field has occurred in the last few years.

In 1975, Venanzi, Zambonelli, and co-workers reported the intramolecular hydroamination of 4-pentenylamine mediated by K_2PtCl_4 [Eq. (11)].[67] Subsequent studies[68] showed



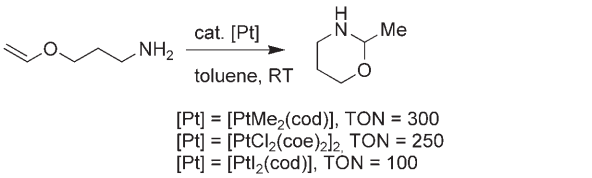
(11)

that six-membered rings could also be formed. Although turnover could be achieved in a batch-type sequence, the slow reaction rate rendered catalysis impractical. The reaction was proposed to proceed through an outer-sphere mechanism, involving nucleophilic attack of amine on the coordinated alkene, as had been previously demonstrated in several stoichiometric studies.[11,12,21,69] Protonolysis of the resulting Pt–C bond would give the cyclic amine product and regenerate the catalyst (Scheme 9).



Scheme 9. Proposed outer-sphere mechanism for the catalytic intramolecular hydroamination.

Recently, significantly more active systems for the platinum-catalyzed hydroamination have been developed, which allows the functionalization of activated and unactivated olefins. For example, aminopropyl vinyl ether can be regioselectively cyclized to give the hemiaminal ether [Eq. (12); cod = cycloocta-1,5-diene, coe = cyclooctene, TON = turnover number].[70] Although up to 300 turnovers can be achieved with $[PtMe_2(cod)]$, palladium catalysts were approximately 5 times more active. The hydroamination of acrylonitrile with *para*-toluidine is catalyzed with moderate efficiency (up to TON = 45) by PCP-pincer complexes of platinum [Eq. (13); Cy = cyclohexyl, Tf = trifluoromethanesulfonyl].[71] An inner-



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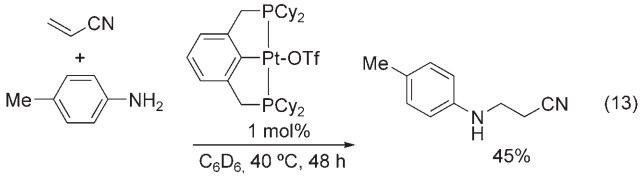
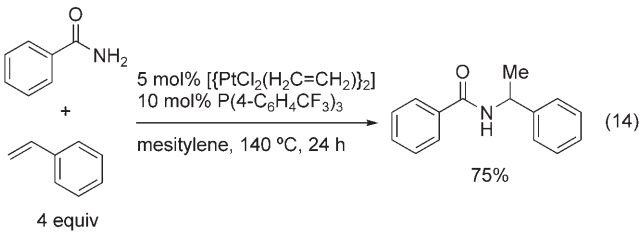


(13)

sphere mechanism was favored that involves the migratory insertion of the C–C bond into a platinum–amido bond rather than nucleophilic attack of the amine at a Pt-coordinated olefin, based on a direct observation of the stoichiometric reaction of [(PCP)PtNH(*p*-tol)] with acrylonitrile to give the β-amino Pt–alkyl species; similar studies into the stereochemistry of addition to crotononitrile would be informative in this case.

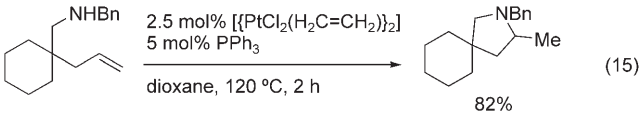
Vinylarenes, for which the palladium-catalyzed hydroamination has recently been extensively explored,[65,72,73] have also been shown to undergo intermolecular platinum-catalyzed hydroamination with carboxamides, albeit at high temperatures [Eq. (14)].[74] Carbamate and sulfonamide



(14)

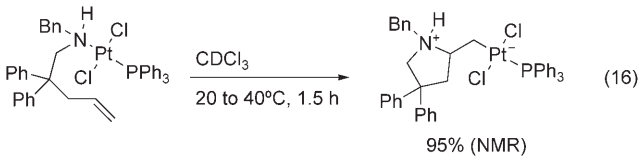
nucleophiles were also successful. An excess of styrene was required to drive the reaction to completion, as ΔG was estimated to be only $-1.5\ \mathrm{kcal\,mol^{-1}}$ at the temperature employed.

Several systems for the platinum-catalyzed hydroamination of terminal aliphatic olefins or ethylene have recently been developed. Bender and Widenhoefer have demonstrated that $[\{PtCl_2(H_2C{=}CH_2)\}_2]/PPh_3$ catalyzes the intramolecular reaction to give five- or six-membered heterocycles [Eq. (15); Bn = benzyl].[75] Substitution with *gem*-dialkyl or



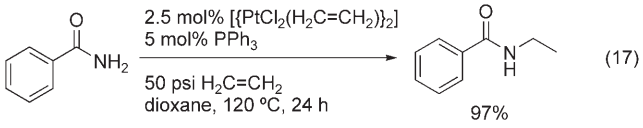
(15)

gem-diaryl groups aided the cyclization, but was not required. Monitoring of a stoichiometric reaction by NMR spectroscopy allowed the observation of the direct conversion of a platinum–amine complex to the β-amino alkyl, a net insertion of C–C into the Pt–N bond [Eq. (16)]. The authors prefer an outer-sphere mechanism that involves the displacement of the amine group by the olefin moiety followed by an intra-



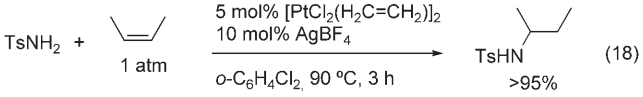
(16)

molecular nucleophilic attack, rather than the direct insertion as proposed above[71] [Eq. (13)]. Wang and Widenhoefer have demonstrated that the same platinum/phosphine system catalyzes the intermolecular hydroamination of ethylene and propylene with amide or carbamate nucleophiles [Eq. (17)].[76]



(17)

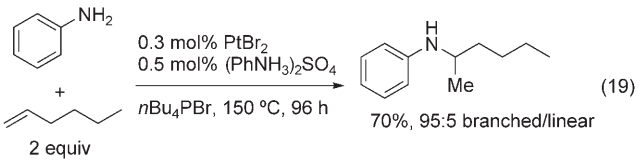
Tilley and co-workers have recently reported a method for the intermolecular platinum-catalyzed hydroamination that proceeds at 90 °C, and is effective for a range of unactivated olefins, which includes propene, *cis*-2-butene, cyclopentene, and cyclohexene [Eq. (18); Ts = 4-toluenesulfonyl].[77] Sul-



(18)

fonamides, carboxamides, and weakly basic anilines (conjugate acid $pK_a < 1$) may be used. Only one equivalent of olefin (or 1 atm for gaseous olefins) is required for full conversion. The precursor $[(cod)Pt(OTf)_2]$ was a somewhat less active catalyst, but allowed mechanistic studies to be performed on the hydroamination of norbornene with 4-butylbenzenesulfonamide. The catalyst resting state is $[(cod)Pt(norbornene)_2]^{2+}$, and kinetics studies indicated that the reaction is first order in platinum complex and sulfonamide, but zero order in olefin. Based on these observations, an outer sphere mechanism was proposed, involving rate-determining nucleophilic attack of sulfonamide on the platinum-coordinated olefin, followed by fast protonolysis of the resultant Pt–C bond, then binding of a new molecule of olefin to complete the catalytic cycle. A mechanism that involves a fast reversible nucleophilic attack followed by a rate-determining proton transfer is also consistent with the kinetic data.

The use of ionic solvents for chemical reactions has grown significantly in recent years.[78,79] In addition to their low volatility, which offers a potential environmental benefit, ionic liquids are extremely polar and usually aprotic, often resulting in unique reaction efficiencies or selectivities. Brunet and co-workers have developed a system for the addition of anilines to alkenes catalyzed by $PtBr_2$ that functions particularly well in the ionic solvent nBu$_4$PBr.[80] An increase in catalytic efficiency for this solvent was also observed for Rh-catalyzed hydroamination. The platinum system was effective for the high-temperature hydroamination of norbornene,[80] ethylene,[81] and 1-hexene.[82] The selective Markovnikov hydroamination of 1-hexene [Eq. (19)] is significant, as rapid Pt-catalyzed olefin isomer-

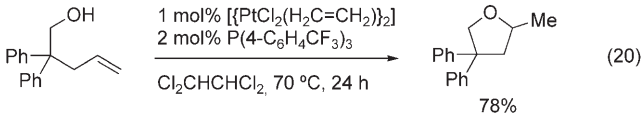


(19)

ization is common, and was observed by Tilley and co-workers.[77] Although the precise reason for the benefit of nBu$_4$PBr as solvent is unknown, the high concentration of bromide ions in the reaction medium seems important as reactions in nBu$_4$PCl were much less effective. It was proposed that coordinated bromide ion increases the basicity of the platinum center, thus facilitating protonolysis of the M–C bond after addition of the amine to the Pt-complexed olefin. Alternatively, they suggest that poisoning of the catalyst by the amine may be reduced by coordination of the bromide ion.

3.2. Oxygen Nucleophiles: Platinum-Catalyzed Hydroalkoxylation of Alkenes

In the sole example of platinum-catalyzed hydroalkoxylation, Widenhoefer and co-workers have shown that $[\{PtCl_2(H_2C\text{-}CH_2)\}_2]/2P(4\text{-}C_6H_4CF_3)_3$ is an effective catalyst for the cyclization of a range of γ- and δ-hydroxyolefins under mild conditions [Eq. (20)].[83] The system is generally selective

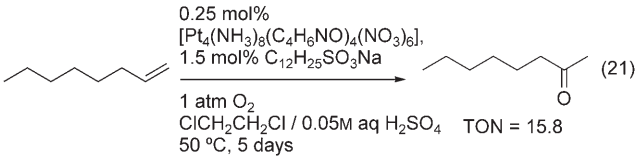


(20)

for oxygen addition to the more highly substituted carbon atom, and five- or six-membered rings may be formed. The selectivity for hydroalkoxylation (oxyplatination followed by Pt–C protonolysis) in the platinum system contrasts markedly with palladium-based systems, which tend to give oxidized products through a Wacker-type oxypalladation/β-hydride elimination mechanism.[84–86]

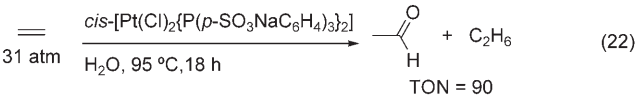
3.3. Oxygen Nucleophiles: Platinum-Catalyzed Wacker Oxidation of Alkenes

Although the Wacker oxidation of alkenes to ketones and aldehydes is dominated by palladium catalysis,[87] platinum catalysts are also competent, albeit with significantly reduced efficiency. Matsumoto and co-workers[88,89] reported that tetranuclear platinum blue complexes and dinuclear Pt^{III} complexes catalyze the oxidation of terminal olefins to ketones, with O_2 as the only oxidant [Eq. (21)]. Approximately 10 to 20 turnovers were generally observed. Cyclic



olefins were oxidized mainly to epoxides. The oxygen atom that is incorporated into the products comes exclusively from water and no deuterium is incorporated when D_2O is used. These observations led to the conclusion that the mechanism of the olefin oxidation is similar to that established for the Pd-catalyzed Wacker oxidations, and consists of the attack of H_2O on a Pt-coordinated alkene, followed by loss of ketone to give a platinum hydride, which is then oxidized by O_2 to regenerate the catalyst.

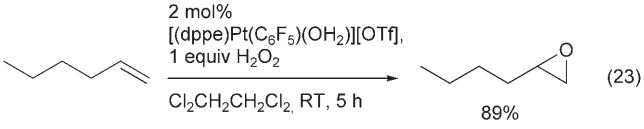
Helfer and Atwood[90] recently reported that water-soluble platinum–phosphine complexes catalyze the aqueous oxidation of ethylene to acetaldehyde under an atmosphere without oxygen [Eq. (22)]. The required oxidative equivalent



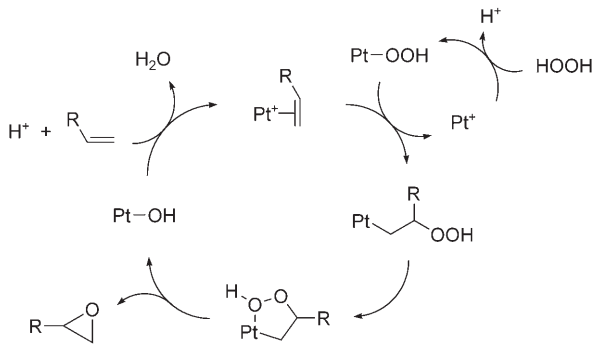
is provided by ethylene, which acts as a hydrogen acceptor to produce ethane. Mechanistic experiments including the use of C_2D_4 or D_2O indicate that the mechanism of acetaldehyde production is analogous to the Pd-catalyzed Wacker oxidation. At room temperature a stoichiometric reaction was observed that produced one equivalent of acetaldehyde and one equivalent of a platinum–ethyl complex, which was formed by insertion of ethylene into the Pt–H bond. Protonolysis of this intermediate would complete the catalytic cycle.

3.4. Oxygen Nucleophiles: Platinum-Catalyzed Epoxidation of Alkenes

The research group of Strukul has shown that cationic $Pt(OH)_2$ complexes catalyze the highly selective epoxidation of terminal olefins when H_2O_2 is used as the oxidant [Eq. (23); dppe = ethane-1,2-diylbis(diphenylphosphane)].[91–93]



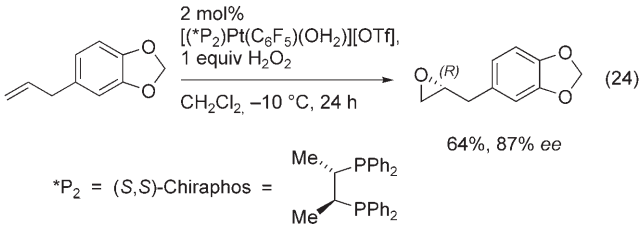
Kinetic analysis indicates that the reaction rate is second order in platinum complex, which was proposed to originate from dual activation of the olefin and the nucleophile (HOO^-), by different platinum atoms.[94] The mechanism shown in Scheme 10 was proposed and incorporates evidence from the observation of catalytic intermediates. The key step



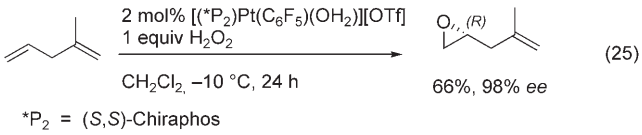
Scheme 10. Proposed mechanism for Pt-catalyzed epoxidation of terminal olefins.

involves the bimolecular reaction of a Pt–OOH species (generated by the reaction of H_2O_2 with Pt^+) with a cationic Pt–olefin species to give a β-peroxyalkyl–Pt species, which forms a five-coordinate platinacycle by coordination with the oxygen atom, and finally collapses to give the epoxide and Pt–OH. Ligand substitution regenerates the starting Pt–olefin complex.

Recently, an enantioselective version of this transformation was reported.[95] A series of terminal olefins gave enantiomeric excess values that ranged from 58% to 98% for the epoxidation when (*S*,*S*)-chiraphos was employed as the ligand [Eq. (24)]. This method is promising, as the catalyst

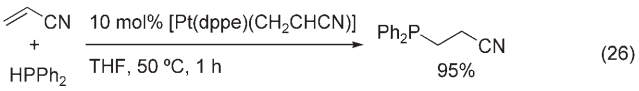


is completely selective for the epoxidation of terminal olefins; 1,2- or 1,1-disubstituted alkenes are left untouched under the conditions reported [Eq. (25)]. These results highlight the potential of platinum(II) catalysts for the selective activation of less-hindered alkenes, as catalysts for electrophilic epoxidation typically favor more highly substituted electron-rich olefins.[96]



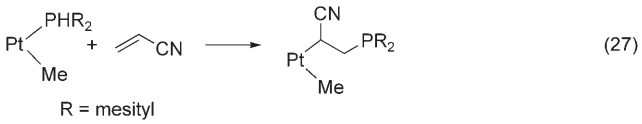
3.5. Phosphorus Nucleophiles: Platinum-Catalyzed Hydrophosphination of Activated Alkenes

The research group of Glueck has described platinum(0) complexes that catalyze the addition of primary and secondary phosphines to activated olefins such as acrylonitrile and *tert*-butylacrylate [Eq. (26)].[97,98] Phosphines were shown to



(26)

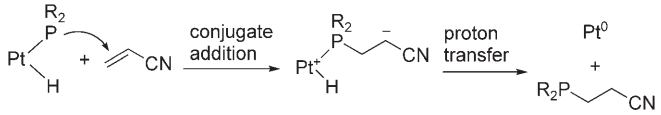
oxidatively add to the Pt^0 precatalysts to give Pt^{II} phosphido hydrides, which released the hydrophosphinated organic product and the starting Pt^0 complex on treatment with acrylonitrile. Model Pt^{II} phosphido complexes, which lacked a hydride ligand, were shown to give the products of formal insertion of acrylonitrile into the Pt–P bond [Eq. (27)].



(27)

Originally, a mechanism analogous to Scheme 3 was proposed, in which the initial P–H oxidative addition to Pt^0 is followed by a regioselective alkene insertion into the Pt–P bond, and subsequent C–H reductive elimination releases the product to complete the catalytic cycle.

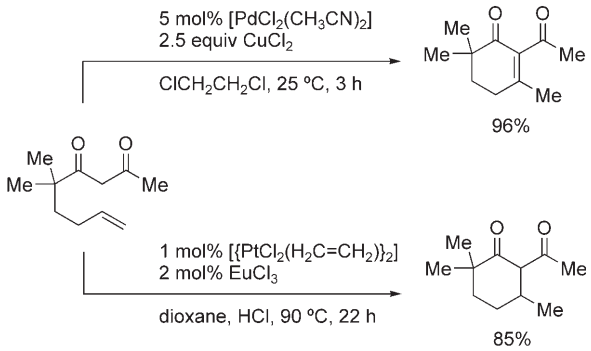
Along with the 1:1 hydrophosphination product, and strongly depending on the solvent polarity, varying amounts of oligomers, incorporating multiple alkene groups, are formed. According to the above mechanism, oligomers would be formed by the insertion of additional alkene molecules prior to the reductive CH elimination. Recently, the addition of *tert*-butylalcohol or water was found to suppress the formation of oligomers.[99] This observation led to the proposal of an alternative Michael-type mechanism, in which the nucleophilic platinum–phosphido species adds to the alkene to give a zwitterionic intermediate that may release product by proton transfer from the platinum to the β-carbon atom (Scheme 11). In this mechanism, the alcohol would function as an acid catalyst for the proton transfer/reductive elimination step. Recent studies, which include the trapping of the putative zwitterionic intermediate with benzaldehyde, have provided further support for this mechanism.[100] In this transformation, platinum does not function to activate the alkene, as in the majority of the reactions discussed in this review, but to activate the nucleophile by oxidative addition. This is consistent with the use of an electron-rich Pt^0 precatalyst.



Scheme 11. Michael-type mechanism for the formation of the P–C bond.

3.6. Carbon Nucleophiles: Platinum-Catalyzed Hydroalkylation of Alkenes

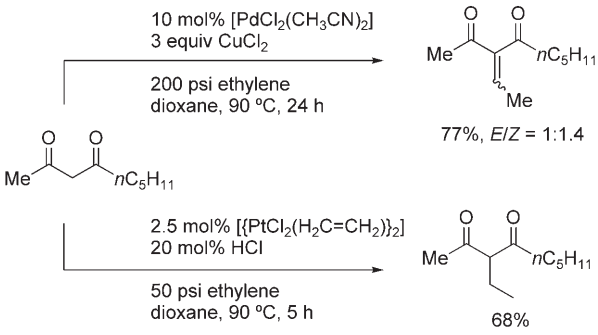
The research group of Widenhoefer has developed and extensively studied the palladium-catalyzed intramolecular addition of stabilized carbon nucleophiles, which include β-diketones, β-ketoesters, and simple dialkyl ketones, to unactivated alkenes.[56,101–104] While $[PdCl_2(MeCN)_2]$ was highly effective for 6-*endo* cyclization, attempts at 6-*exo* cyclization gave oxidized olefinic products,[103] presumably because β-elimination followed by product displacement is more rapid than the protonolysis of the Pd–C bond (see Section 2.3). When palladium was replaced with platinum, the development of an effective method for the hydroalkylation/cyclization of 4-pentenyl β-dicarbonyl substrates was allowed, aided by the addition of HCl and $EuCl_3$ (Scheme 12).[55] It was



Scheme 12. Catalytic cyclization of a 4-pentenyl β-dicarbonyl compound: Pd promotes the oxidation step (top) while Pt promotes the hydroalkyation reaction (bottom).

proposed that HCl aids the protonolysis of the Pt–C bond, and $EuCl_3$ stabilizes the enol tautomer of the substrate, thus facilitating nucleophilic attack on the Pt-coordinated olefin. The beneficial effect of the use of a lanthanide-based Lewis acid was noted previously by Yang et al. in related palladium catalysis.[105] Stereochemical labeling studies on the palladium systems have indicated that carbopalladation occurs exclusively by an mechanism, which involves the *anti* outer-sphere attack of the nucleophile on a coordinated alkene (see Scheme 4).

A similar complementarity between Pd and Pt catalysis was observed for the intermolecular addition of β-diketones and β-ketoesters to ethylene and propylene.[106] Again, Pd systems tended to give oxidized products by β-elimination, and these products could be obtained exclusively in the presence of $CuCl_2$. Conversely, a Pt/HCl system gave hydroalkylation products exclusively (Scheme 13). Although M–C bond protonolysis can clearly predominate over β-elimination

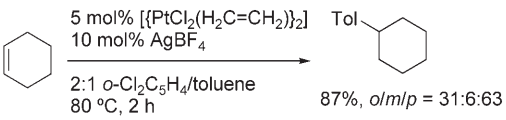


Scheme 13. Addition of a β-diketone to ethylene: Pd promotes the oxidation step (top) while Pt promotes the hydroalkyation reaction (bottom).

in some palladium-catalyzed systems, it appears that platinum–alkyl intermediates are particularly reluctant to undergo β-elimination, thus allowing the development of a broader range of catalytic systems that terminate with M–C bond protonolysis.

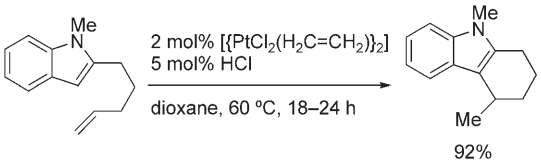
3.7. Carbon Nucleophiles: Platinum-Catalyzed Hydroarylation of Alkenes

The metal-catalyzed hydroarylation of olefins is potentially an extremely useful method to construct substituted aromatics.[107–109] Recently, Tilley and co-workers have demonstrated that highly electrophilic platinum complexes catalyze the hydroarylation of a range of unactivated olefins (2-butene, propylene, cyclopentene, cyclohexene) with simple arenes (benzene, toluene) [Eq. (28)].[110] Both the Markovnikov selectivity for addition to propylene and the *ortho*/*para* selectivity observed for hydroarylation with toluene point to a Friedel–Crafts type of mechanism, which involves electrophilic activation of the olefin on coordination to platinum, and outer-sphere nucleophilic attack by the arene.



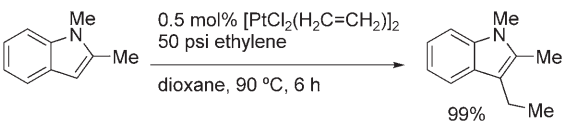
(28)

Widenhoefer and co-workers have reported a method for the platinum-catalyzed hydroarylation/cyclization of alkenylindoles to give tetrahydrocarbazoles [Eq. (29)].[23] Products of



(29)

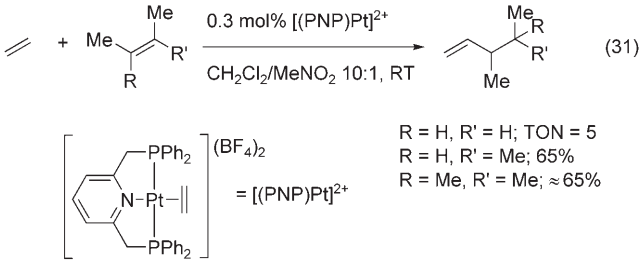
6-*exo* or 6-*endo* cyclization may be obtained, and labeling studies with deuterium indicated that carboplatination of the double bond occurs with *anti* selectivity, consistent with an outer-sphere mechanism of indole attack on a Pt-coordinated olefin followed by Pt–C bond protonolysis (see Scheme 5, Section 2.1). Recently, an asymmetric version of this reaction was reported; enantiomeric excess values of up to 90% were obtained.[111] The intermolecular addition of indoles to ethylene, propylene, 1-butene, and vinylarenes has also recently been reported [Eq. (30)].[112] Although a palladium-catalyzed analogue of this reaction has not been demonstrated, palladium-catalyzed oxidative cyclizations of alkenylindoles terminated either by β-elimination[24,113] or by methoxycarbonylation[114] have been reported. Interestingly, stereochemical studies into a palladium system support a mechanism that consists of an indole C–H bond activation, *syn* insertion of the olefin, and β-hydride elimination,[24] in contrast to the mechanism of olefin activation in the platinum system.



(30)

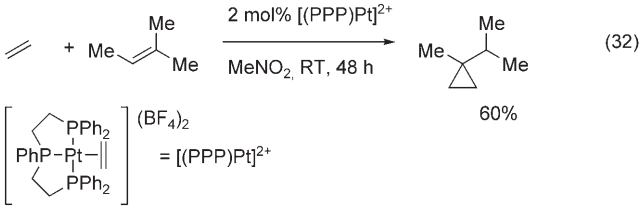
3.8. Carbon Nucleophiles: Platinum-Catalyzed Hydrovinylation and Diene Cycloisomerization

In 1976, Panunzi and co-workers reported that the dicationic complex $[Pt(MeCN)_4](BF_4)_2$ catalyzed the dimerization of several branched olefins, although few details were given.[115] Vitagliano and co-workers recently reported that a dicationic pincer complex of platinum catalyzed the selective codimerization of ethylene with several internal olefins to give products of hydrovinylation with *cis*-2-butene or 2-methyl-2-butene, or of carbovinylation with tetramethylethylene [Eq. (31)].[116]

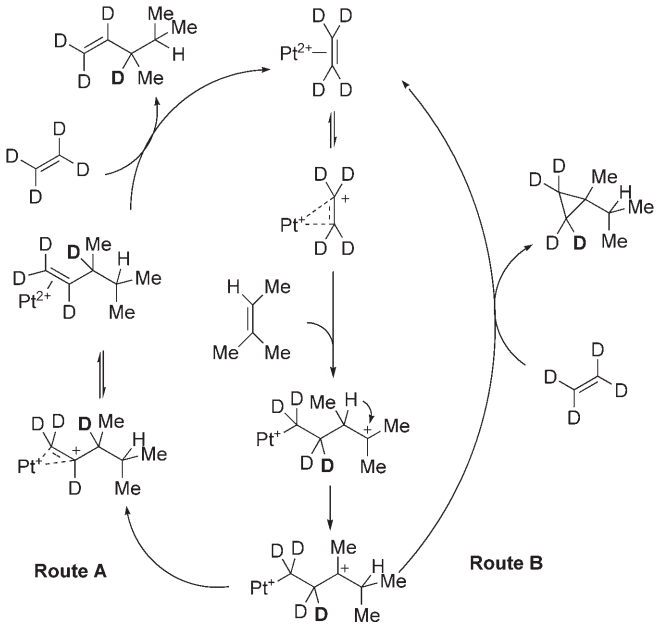


(31)

By a simple change in ligand, cyclopropanes alternatively may be formed by a platinum-catalyzed intermolecular olefin dimerization [Eq. (32)].[117] In the proposed mechanisms for these transformations, both reactions are initiated by the attack of an electron-rich tri- or tetrasubstituted olefin on a Pt-coordinated ethylene molecule (Scheme 14). This generates a δ-carbocationic platinum alkyl species, which rearranges by a 1,2-hydride shift to give a γ-carbocation. Here, the paths diverge depending on the ligand on Pt. For the PNP pincer ligand, a subsequent 1,2-hydride shift generates the hydrovinylation product as a Pt–olefin complex (Route A), which was observed by NMR. Displacement of product by ethylene completes the catalytic cycle. When the PPP ligand triphos is employed, the γ-cationic Pt–alkyl intermediate is trapped by the Pt–C bond to release the observed cyclopropane product (Route B). Experiments using deuterated



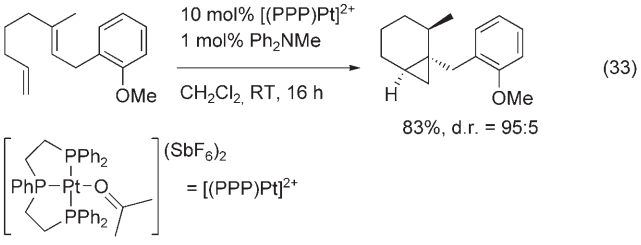
(32)



Scheme 14. Mechanism of hydrovinylation and cyclopropanation in the Pt-catalyzed alkene dimerization.

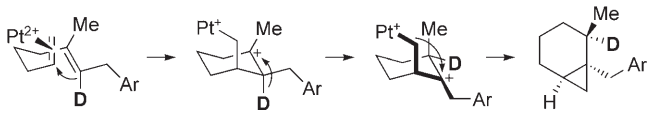
ethylene support both the proposed mechanistic schemes. Notably, the mechanism for hydrovinylation contrasts sharply with that for the related reactions catalyzed by more electron-rich metal complexes.[118] It was proposed that the selectivity may be related to the different *trans* influence of the central donor atom on each ligand; the hydride shift to give an olefin complex (Route A) may be preferred when the resulting Pt–olefin complex is more stable, as would be the case for a nitrogen donor atom with lower *trans* influence. Conversely, a *trans* donor atom with higher *trans* influence (phosphorus) might be expected to increase the basicity of the Pt–C bond, which would favor the trapping of the γ-cation by cyclopropanation (Route B).

Gagné and co-workers have recently reported the intramolecular activation of a terminal olefin toward attack by a tethered trisubstituted olefin.[119] In the presence of a dicationic platinum complex, 1,6-dienes were shown to undergo a cycloisomerization reaction to give [4.1.0] bicyclic products [Eq. (33)]. The proposed mechanism, supported by labeling studies with deuterium, is shown in Scheme 15. Initial



(33)

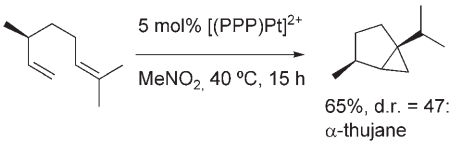
coordination of the terminal alkene to the Pt center promotes the nucleophilic attack of the trisubstituted alkene to give a δ-carbocationic Pt–alkyl complex; a subsequent 1,2-hydride



Scheme 15. Proposed mechanism for diene cycloisomerization terminated by cyclopropanation.

shift followed by trapping of the γ-cation by the Pt–C bond generates the cyclopropane product.

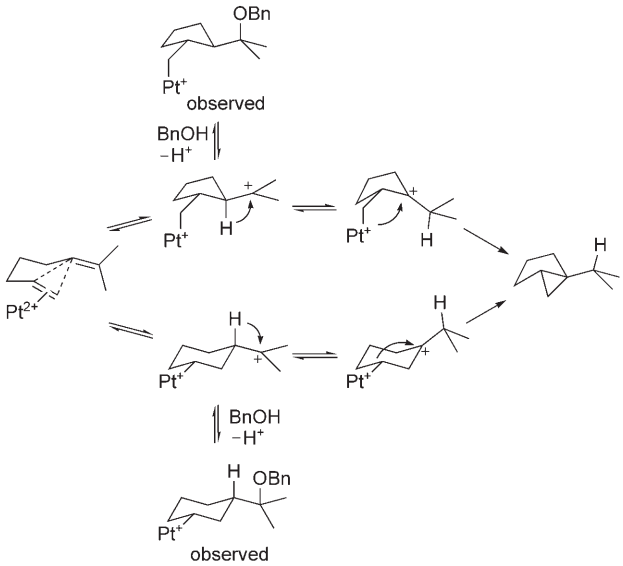
The formation of [3.1.0] bicyclic products was allowed on adjusting the substitution at the olefin. Only products that resulted from cation formation at the tertiary carbon atom were observed, for example the conversion of β-citronellene into α-thujane in Equation (34).[120] Experiments that



(34)

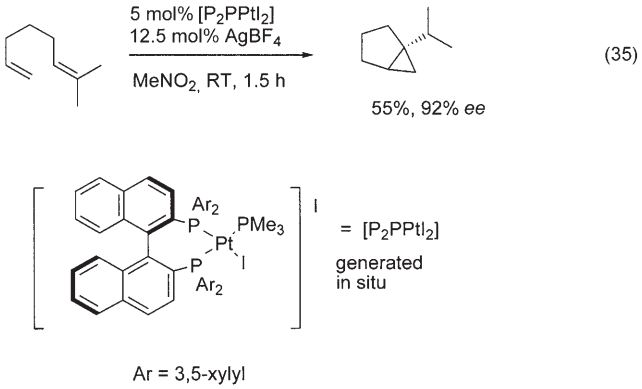
employed benzyl alcohol as a cation-trapping nucleophile supported the mechanistic proposal, as δ-benzyloxyalkyl–platinum species were formed reversibly (Scheme 16). As either initial 5-*exo* or 6-*endo* cyclization in principle can lead to the [3.1.0] products, the precise mechanism of product formation is as yet unclear. As was pointed out by Vitagliano and co-workers,[116] the use of pincer ligands inhibits the β-hydride elimination from Pt–alkyl intermediates that could potentially lead to side products.

As modulation of pincer-type ligands poses a significant synthetic challenge, efforts have recently been directed at the possibility of combining easily available bidentate and



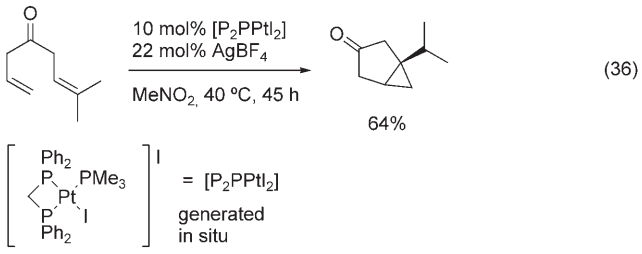
Scheme 16. Two possible pathways for cycloisomerization/cyclopropanation of 1,6-dienes. The trapping experiments with benzyl alcohol indicate that both 6-*endo* and 5-*exo* cyclizations occur reversibly, but it is unclear whether one or both reaction pathways lead to the product.

monodentate ligands to occupy three coordination sites on the platinum center. These investigations have resulted in the development of a highly enantioselective catalytic system that is generated in situ and employs enantiopure (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) (binap) and trimethylphosphine as ligands [Eq. (35)].[121] Catalysts that employed only



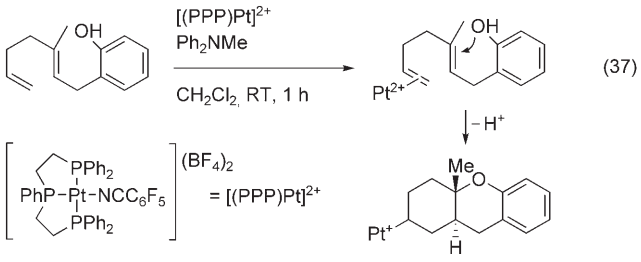
(35)

[(binap)PtI_2] and $AgBF_4$ were also active catalysts for this reaction; interestingly, the sense of enantioselectivity is reversed when PMe_3 is removed from the system. Although the blocking of three coordination sites on the Pt center is not a requirement for the observed cycloisomerization chemistry, catalysts that contained only a bidentate ligand were not as selective or general as those generated by a combination of bidentate and monodentate ligands. An achiral platinum catalyst formed from (bis(diphenylphosphino)methane) (dppm) and trimethylphosphine was found to be exceptionally active for this transformation, and allows the cycloisomerization of more difficult substrates that contain Lewis basic functionality [Eq. (36)].[121]



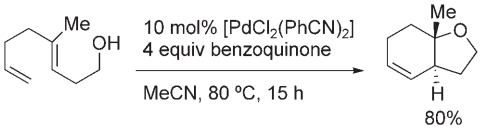
(36)

Additional supporting evidence for the intermediacy of carbocations comes from the stoichiometric metal-mediated cyclization of dienes with a tethered protic nucleophile positioned appropriately to trap the cation [Eq. (37)].[22] Dicationic Pt- or Pd-pincer complexes (not shown) promote the bicyclization of dienylphenols to give cationic metal alkyls. Catalytic turnover has not yet been observed, as the tridentate ligand prevents β-hydride elimination and the complexes are too weakly basic to release product by Pt–C bond protonolysis. However, [$PdCl_2$(PhCN)$_2$] promotes a mechanistically analogous oxidative catalytic process, in which the bicyclization step is followed by the β-hydride



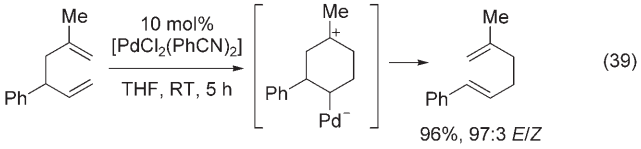
(37)

elimination, and the palladium is reoxidized by benzoquinone [Eq. (38)].[122] The stereochemistry of the polycyclization



(38)

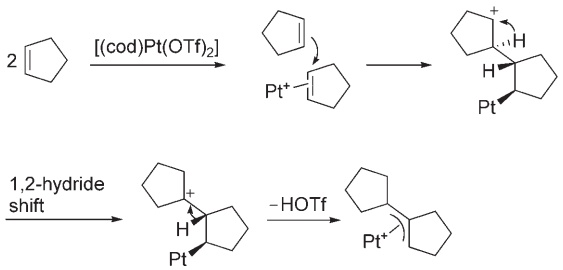
products provides evidence for an *anti* addition to the alkene moieties, as opposed to a coordination and *syn* insertion [see Eq. (4), Section 2.1]. Carbocationic intermediates such as those shown above were postulated earlier in the Pd-catalyzed Cope rearrangement of 1,5-dienes, developed by Overman et al. [Eq. (39)].[123] The transfer of stereochemistry



(39)

was consistent with a chair conformation of the cyclic carbocationic intermediate,[124] and a study of substituent effects supported the proposed intermediacy of a carbocation.[125]

Szuromi and Sharp have recently demonstrated that several alkenes undergo stoichiometric dimerization in the presence of [(cod)Pt(OTf)$_2$] to give Pt–alkyl or Pt–π-allyl complexes, with the elimination of triflic acid (Scheme 17).[126] It was proposed that the reactions proceed by either vinylic C–H bond activation followed by olefin insertion (not shown), or by outer-sphere attack of one olefin on a complexed olefin followed by elimination of HOTf from a

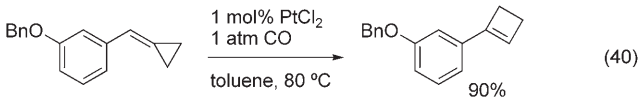


Scheme 17. Stoichiometric dimerization of cyclopentadiene and elimination of HOTf to give a Pt–π-allyl complex.

carbocationic intermediate. The generation of Pt–alkyl or Pt–π-allyl complexes by olefin dimerization and acid elimination may provide a useful model for the future development of catalytic transformations based on the activation of olefins.

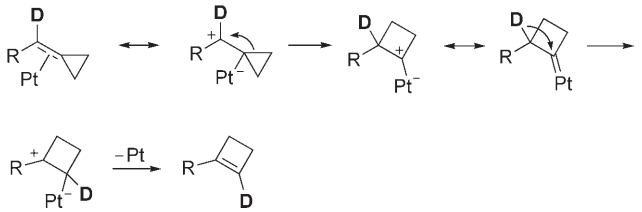
3.9. Platinum-Catalyzed Ring-Expansion Reactions Initiated by Olefin Activation

In a recent development, Fürstner and Aïssa have reported that methylenecyclopropanes are converted selectively into cyclobutenes in the presence of $PtCl_2$ under an CO atmosphere [Eq. (40)].[127] Both aryl and alkyl substitution at



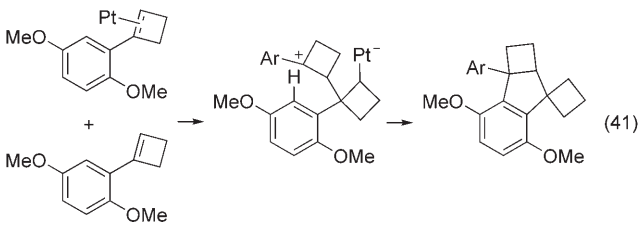
(40)

the alkene is tolerated. Although CO is not incorporated into the product, the catalytic efficiency was improved significantly in its presence and probably is due to the highly electron-withdrawing nature of the CO ligand, which presumably renders the platinum center more electrophilic. The pathway shown in Scheme 18 was proposed: the coordination



Scheme 18. Proposed mechanism for the ring-expansion of methylenecyclopropanes.

of the olefin to platinum activates the substrate toward ring expansion to give a four-membered ring with Pt-carbene character, and a 1,2-hydride shift generates the product. Labeling studies with deuterium supported the proposed mechanism. Electron-rich substrates underwent a further reaction to give dimerized products, which resulted from the attack of the cyclobutene product to a second Pt-complexed product, followed by intramolecular attack of the arene on the generated carbocation, and termination by proton transfer [Eq. (41)]. A recent report demonstrates that a $Pd(OAc)_2$/$CuBr_2$ system also catalyzes transformations analogous to

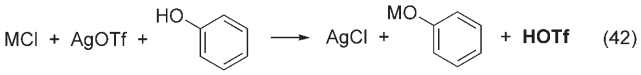


(41)

those in Equation (40), although a different mechanism was proposed.[128]

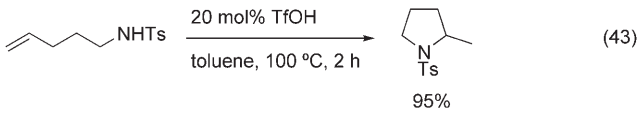
4. Acid-Catalyzed Additions to Alkenes

One aspect of the platinum-catalyzed electrophilic activation of olefins that becomes apparent in comparison with the related palladium systems is that platinum often functions as a Lewis acid or simple electrophile, whereas palladium more often promotes elementary steps more traditional to classic organometallic chemistry, such as oxidative addition/reductive elimination and 1,2-migratory insertion/β-elimination. As a result, special care should be taken to rule out the occurrence of Brønsted acid catalysis with appropriate control reactions. This pitfall is of course not unique to platinum, however, as the combination of any strong Lewis acid with a mild protic acid (including trace water) can in principle result in the generation of strong protic acid [for example, Eq. (42)].



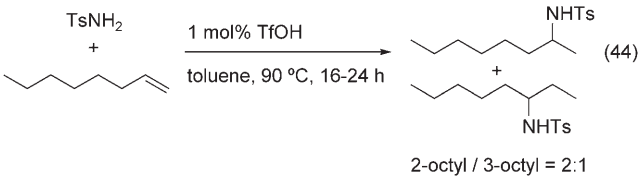
(42)

Several recent studies have highlighted the capability of H^+ to catalyze transformations related to some of the addition reactions described in this review, under quite mild conditions. Schlummer and Hartwig showed that the intramolecular hydroamination of styrenes and unactivated olefins, including terminal olefins, can proceed in the presence of 20 mol% trifluoromethanesulfonic acid or sulfuric acid [Eq. (43)].[60] Intermolecular variants have been shown to



(43)

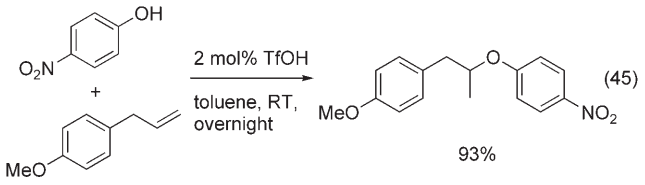
proceed with only 1 mol% TfOH [Eq. (44)].[129] Hartwig and co-workers suggested control experiments, suitable for inter-



(44)

or intramolecular reactions, to distinguish acid catalysis from metal catalysis, that are based on the competitive hydroamination or hydroalkoxylation of different olefin moieties with the same nucleophile.

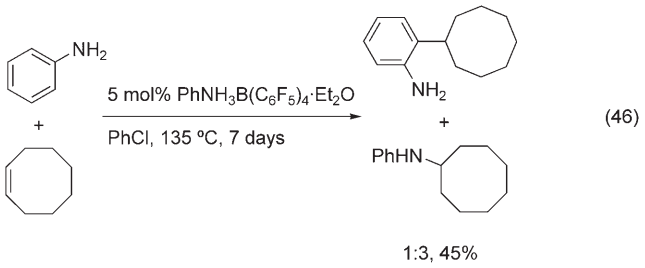
The intermolecular addition of oxygen and nitrogen nucleophiles to alkenes catalyzed by TfOH was recently demonstrated by He and co-workers [Eq. (45)].[130] Suitable



(45)

nucleophiles include phenols, carboxylic acids, and tosylamides, and a variety of substitution patterns on the olefin are tolerated. It was noted that complete decomposition can occur if reaction conditions are too harsh (for example, 85 °C instead of room temperature or higher acid loading).

Bergman and co-workers have demonstrated that norbornene, styrenes, and cyclic 1,2-disubstituted olefins are reactive toward hydroamination and hydroarylation in the presence of a rather weak anilinium acid [Eq. (46)].[61]



(46)

These results highlight the importance of verifying whether catalytic transformations based on alkene activation are in fact catalyzed by metals or by acid generated under the reaction conditions employed.

5. Summary and Outlook

Platinum is exceptional among Lewis acids in its ability to promote the catalytic outer-sphere addition of nucleophiles to alkenes. As a result of the strong metal–ligand bonds and slow ligand substitution reactions generally observed for platinum, multiturnover cases are predominantly those where the products of *anti* attack may be removed from the metal center without extensive metal–ligand substitution chemistry. Examples described in this review include catalytic turnover by M–C bond protonolysis, cation rearrangements, and cyclopropanation chemistry. When metal–ligand exchange is needed, reactivities are often poor in comparison with palladium catalysis. For example, platinum catalysts for the Heck reaction are rather inefficient, despite a fast oxidative addition step.[131] Also, the slow ligand substitution following β-hydride elimination probably inhibits the development of highly efficient platinum-based catalysts for oxidative tranformations, including the Wacker reaction.

On the other hand, the slow rates of metal-based reactions can be advantageous in some situations. For example, problematic competitive alkene isomerizations can be more easily suppressed. Palladium analogues of the platinum catalysts discussed in Section 3.8 more efficiently catalyze olefin isomerization than cyclopropanation. Similarly, as rates of β-hydride elimination are generally reduced, the development of catalytic pathways with a variety of other turnover mechanisms (for example, cyclopropanation) is potentially more feasible. The result is that palladium and platinum catalysts are often complementary in the transformations they facilitate.

So in many ways, platinum(II) functions more as a Lewis acid than palladium(II), but it is a Lewis acid with special properties. Clearly, the ability to vary the ancillary ligands provides opportunities for electronic and steric control of selectivity, including enantioselectivity. While many electrophiles, including H^+, Al^{III}, and Sn^{IV}, preferentially activate more highly substituted alkenes as a result of the stability of the resulting carbocations, transition metals tend to bind and activate less substituted alkenes because of their reduced steric bulk, thus offering an inherent selectivity that is complementary to main-group Lewis acid catalysis. Finally, the kinetic stability of the Pt–C bond to β-hydride elimination opens a myriad of possibilities for its alternative functionalization that have only begun to be exploited.

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[8] In the mechanistic schemes shown in this Review, metal complexes are depicted with only the reactive ligands (bound substrate); ancillary ligands that may or may not be bound are not shown. The oxidation state of the metal (M) is explicitly represented for M^0 and M^{IV} states; otherwise, the oxidation state is +2. The charges shown may be arbitrary (but are consistent throughout a single scheme), as the presence or absence of anionic ancillary ligands is not always clear.
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