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Invited review

The organometallic chemistry of nitrogenases

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Abstract

Nitrogenases mediate the reduction of many substrates other than dinitrogen and a summary is given. Several chemical systems that mimic aspects of nitrogenase reactivity, including transition metal complexes of alkynes and olefins, are outlined. Their protonation has been studied and their relevance to reduction of alkynes and olefins by nitrogenase is assessed. Cyclopropene is reduced by molybdenum nitrogenase to propene and cyclopropane. The reactions of cyclopropene with different transition metal complexes are discussed and a study of interactions of cyclopropenes with models for the active site of the nitrogenase enzyme are described. These models include transition metal hydrides, such as $[FeH(H_2)(dmpe)_2][BPh_4]$ and $[MoH_4(dppe)_2]$ reducing 3,3-dimethylcyclopropene and cyclopropene. Products observed upon protonation and deuteration of several platinum–cyclopropene complexes are presented and a mechanism for their formation is proposed.

Keywords: Cyclopropene; Molybdenum; Titanium; Iron; Vanadium; Nitrogenases

1. Introduction

The participation of metal–carbon bonds in the chemistry of living things has been recognised for many years even though it is exceedingly rare. The function of the vitamin B_{12} co-enzyme apparently involves cobalt–carbon bonds [1]. Very recently, the participation of molybdenum–carbon bonds in the action of xanthine oxidase has been suggested [2]. In contrast, it is unlikely that the metal–carbon bonds are involved in the function of hydrocarbon monooxygenases [3]. Nitrogenase does not undergo obvious metal–carbon chemistry during its primary function, but nevertheless it does appear capable of mediating the reduction of some hydrocarbons [4]. This review is intended to convey what we know about this kind of nitrogenase chemistry, and about the chemical models that have been constructed to try to mimic it.

There are three distinct kinds of nitrogenase, each of which consists essentially of two proteins [5]. The most common "classical" nitrogenase contains iron and molybdenum but more recently two variants which are genetically distinct have been characterised. They are based upon iron and vanadium, and (apparently) upon iron alone, respectively. These three nitrogenases have comparable properties. They each consist of two proteins. One of the proteins, the smaller of the two, in each case contains a four-iron four-sulphur cluster. It apparently functions as an electron-transfer agent to the larger protein. One can carry out fixation experiments with these two proteins by mixing them, with rigorous exclusion of dioxygen, in an appropriately buffered solution which also contains ATP, or an ATP-generating system. This complex mixture can then convert dinitrogen to ammonia. It is also possible, though not with maximum effectiveness, to interchange proteins, so that, for example, the iron protein from a vanadium nitrogenase can interact with the larger molybdenum–iron protein from a molybdenum nitrogenase. The function of the iron protein, in all three cases, appears to be to act as an electron carrier from some external source to the larger protein. The stoichiometry of dinitrogen reduction varies from system to system, for the MoFe system it is, at best, $N_2 + 8H^+ + 8e^- \rightarrow 2NH_2 + H_2$. For the VFe system the corresponding stoichiometry is $N_2 + 12H^+ + 12e^- \rightarrow 2NH_3 + 3H_2$. The all-iron system produces proportionately even more H_2.

The larger proteins in the three nitrogenases seem to be of a similar structure, as judged by their spectral

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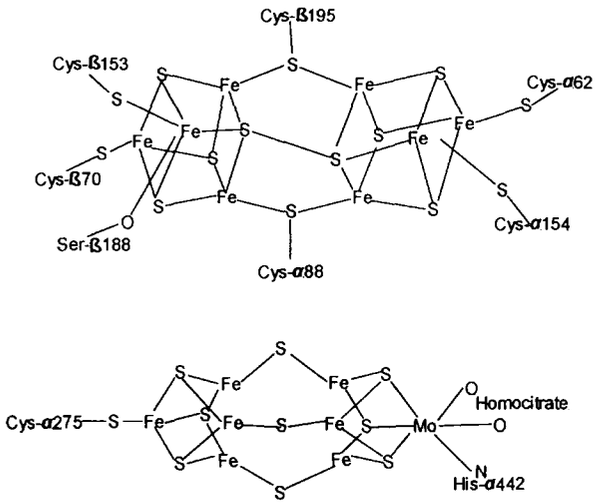


Fig. 1. Schematic representations of the clusters in the MoFe protein of *Azotobacter vinelandii* (see text).

properties [5]. The structures of two variants of the molybdenum–iron protein have been described recently, and they are very similar [6,7]. Although the structures derive from an oxidation level which does not interact with dinitrogen, it is nevertheless surprising that metal clusters of the structures (Fig. 1) give no clear indication of where dinitrogen might be bound, neither do they suggest any clear mechanism of dinitrogen reduction. Nevertheless, the evidence appears to confirm that the MoFe cluster contains the seat of dinitrogen binding and reduction. All this is still open to speculation [8].

It was observed quite early in the study of nitrogenases that these enzymes are capable of reducing substrates other than dinitrogen. A list is given in Table 1. It is difficult to conceive of a single transition metal site which can mediate all these transformations. In our current context, the most interesting observations are that molybdenum nitrogenases can reduce acetylene to ethylene but no further, and that they can also reduce some cyclopropenes. Normally, ethylene is the limit of the reduction, though molybdenum nitrogenases are in some circumstances able to reduce ethylene to ethane in the absence of any substrate other than protons. Some ethane can also be produced if an iron protein from one organism is combined with a MoFe protein from another, and the vanadium nitrogenases also produce some ethane from acetylene. When molybdenum nitrogenases reduce acetylene to ethylene in a deuterated medium, the product is *cis*-1,2-dideuteroethylene [5,9].

Table 1
A list of substrates reduced by nitrogenases

$2H^+ + 2e^- \rightarrow H_2$
$N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2$
$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$
$CN^- + 7H^+ + 6e^- \rightarrow CH_4 + NH_3$
$CH_3NC + 6H^+ + 6e^- \rightarrow CH_3NH_2 + CH_4$
$N_3^- + 3H^+ + 2e^- \rightarrow N_2 + NH_3$
$C_2H_2 + 2H^+ + 2e^- \rightarrow C_2H_4$
$H_2N\text{-}CN + 6H^+ + 6e^- \rightarrow NH_3 + CH_3NH_2$
cyclo-$C_3H_4 + 6H^+ + 2e^- \rightarrow$ cyclo-C_3H_6
cyclo-$CH_2N_2 + 6H^+ + 6e^- \rightarrow CH_3NH_2 + NH_3$
cyclo-3,3-$C_3H_2F_2 + 4H^+ + 4e^- \rightarrow CH_2CFCH_3 + HF$
cyclo-3,3-$C_3H_2F_2 + 6H^+ + 6e^- \rightarrow CH_2CHCH_3 + 2HF$

In many ways cyclopropenes are even more interesting. Cyclopropene is a difficult reagent to manipulate [10], but it is reduced by molybdenum nitrogenases to give cyclopropane and propene [11]. If deuterated systems are used, then the products are mainly *cis*-1,2-dideutererocyclopropane, *cis*- and *trans*-1,3-dideuteropropene, and, more surprisingly, 2,3-dideuteropropene. This last compound must clearly be produced by some hydrogen-shift reactions. In addition 3,3-difluorocyclopropene is also a nitrogenase substrate, and may react to lose fluoride, which also suggests some hydridic character in the nitrogenase active centre [12]. We have also obtained kinetic evidence that both the cyclopropane and the propene are generated from a common intermediate [13]. Finally it has been shown that both methylacetylene and allene, more stable isomers of cyclopropene [14], are reduced by molybdenum nitrogenases to give propene [15]. Consequently, isomerisation, particularly prior to the formation of 1,2-dideuteropropene, cannot be excluded as a component of the cyclopropene reduction reaction [16].

For many years in the Nitrogen Fixation Laboratory (NFL) we have been attempting [17] to develop functional models for nitrogenases, and we shall now discuss our data with respect to the reduction of olefins and cyclopropenes in this context.

2. The protonation of alkynes and olefins

Catalytic hydrogenation has been a subject of enduring interest to organometallic chemists, and it is not intended to review that subject here. We base the discussion on the simple NFL model used to explain nitrogenase function, that is, complexation of the hydrocarbon followed by its protonation, and simply summarise data obtained in systems which currently mimic best the nitrogenase centre, specifically those based upon *trans*-M(diphosphine)$_2$ (M=Mo or W). Most of this work is due to Henderson, who has reviewed [18] the data admirably and succinctly very recently.

Protonation studies [19] on the reaction of $[V(C_5H_5)_2(PhCCPh)]$ with hydrochloric acid have shown that the major hydrocarbon products is *E*-1,2-diphenylethene (85%), the balance being the *Z* isomer. This is explained by rapid initial protonation at the metal, followed by hydride transfer to give a *cis*-vinyl species. The data imply that stereochemistry of the product is defined by the geometry of the vanadium

complex and the site of protonation. It clearly does not imply simultaneous attack by two protons. The vanadium-containing product is $[V(C_5H_5)_2Cl_2]$ [19].

A similar conclusion has been reached [20] from mechanistic studies on complexes *trans*-$[Mo(HCCR)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (R=alkyl or aryl) with HCl. The products are $[Mo(CCH_2R)Cl(Ph_2PCH_2CH_2PPh_2)_2]$ and RCCH. This implies that the second protonation occurs at the carbon atom remote from the molybdenum producing an alkylidene ($=CHCH_2R$) complex which then loses a proton. This protonation generates a carbon–carbon σ-bond which allows free rotation and hence a loss of stereospecificity. One might infer from this that in nitrogenase the second protonation must occur at the metal-bound carbon atom.

Finally, reaction of *trans*-$[Mo(C_2H_4)_2(Ph_2PCH_2CH_2PPh_2)_2]$ with low concentrations of HCl yields *trans*-$[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]$ and ethylene and ethane, the last two in 1 : 1 molar ratio. The proportion of ethylene to ethane increases with acid concentration, so that, at high acid concentrations only ethylene is generated, together with $[MoH_2Cl_2(Ph_2PCH_2CH_2PPh_2)_2]$. The mechanistic interpretation is that the rapid protonation at carbon, leading to an ethyl intermediate and hence to ethane, is important at low acid concentrations, whereas at high acid concentrations protonation at the metal, releasing ethylene, is predominant. Apparently the protonation of analogous allyl complexes yields propene at low acid concentrations and propyne at higher. This can be rationalised in a similar fashion [18,21].

What this means for nitrogenases cannot yet be clear because it is not obvious what constitutes the active site. However, one might conclude that the preferential generation of ethylene rather than ethane suggests that the metal oxidation state is relatively low (no formation of $M=C-CH_2R$) and that the proton supply is such as to allow protonation at the metal prior to transfer to the hydrocarbon, rather than the direct protonation at carbon. It is not evident how this could be facilitated in the nitrogenases.

3. Reduction of cyclopropenes

Cyclopropenes react with metal compounds in a variety of ways [22], most of which involve opening of the ring. However, simple adduct formation has been observed, especially in platinum chemistry [23]. Ring-opening to form a metallacyclobutene or vinyl-carbene complex is not uncommon, but the majority of reactions of cyclopropenes and metal complexes involve ring-opening and polymerisation *via* oxidative addition, especially with early transition metal compounds, and the hydrocarbon-containing products are often non-volatile. Such reactions are unlikely to parallel those observed with nitrogenase.

Our strategy has been to adapt the functional model used for nitrogen fixation by nitrogenase, which involves coordinating dinitrogen to a metal, followed by protonation of the coordinated dinitrogen coupled with electron flow from the metal to neutralise the charge [24]. Our later work has also involved metal hydrides [25], especially because of the evidence that the active metal site of nitrogenases is hydridic.

Simple complex formation by cyclopropene is relatively rare. Ring-opening, presumably by electrophilic attack by a Lewis acid at a carbon–carbon single bond is much more common. Most simple adducts so far described in the literature are of platinum(0), prepared by reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with the cyclopropene [23,26]. Adducts of cyclopropene, C_3H_4 itself, 3-methylcyclopropene, 1,2- and 1,3- and 3,3-dimethylcyclopropene, and 1,2,3- and 1,3,3-trimethylcyclopropene have been described. They react with CS_2 to regenerate the cyclopropene and it has been suggested that they could be used as storage compounds for the otherwise unstable hydrocarbons. Additional compounds prepared by us are listed in Table 3.

The X-ray crystal structures of $[Pt(PPh_3)_2(3\text{-}MeC_3H_3)]$ and of $[Pt(PPh_3)_2(1,2\text{-}Me_2C_3H_2)]$ have been described [27], and we have also obtained structures for $[Pt(PPh_3)_2(3,3\text{-}Ph_2C_3H_2)]$ and $[Pt(PPh_3)_2(1,2\text{-}Ph_2C_3H_2)]$. Selected structural data are collected in

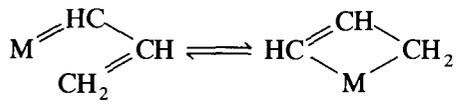
Table 2
Crystallographic data for platinum(0) cyclopropene complexes

X in $[(PPh_3)_2PtX]$	d(C=C) (Å)	d(Pt–C) (Å)	d(cyclopropene C–C) (Å)	d(Pt–P) (Å)	Cyclopropene angle [a] (°)
1,2-Dimethylcyclopropene	1.5	2.12	1.54	2.278	115.8
		2.11	1.55	2.288	
3-Methylcyclopropene	N.A. [b]	1.98	N.A. [b]	2.26	N.A. [b]
		2.21		2.26	
3,3-Diphenylcyclopropene	1.43	2.68	1.52	2.28	123
		2.65	1.51	1.83	
1,2-Diphenylcyclopropene	1.47	2.09	1.54	2.27	113
		2.12	1.50	2.27	

[a] Angle of cyclopropene out of Pt square plane.
[b] Not available.

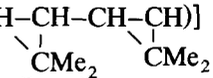
Table 2. The coordination in all the compounds is similar, with the cyclopropene forming an approximate square-plane about the platinum, but with the cyclopropene ring making an angle with the coordination plane of ca. 118°. The C=C bond is lengthened in every case with respect to the free cyclopropene (1.45 compared with 1.30 Å) and the Pt–C bonds are all of about the same length. Analogous compounds for palladium(0) are not known, though the 2,3,3-trimethyl- and tetramethyl-cyclopropene complexes, $[Ni(PPh_3)_2(C_3Me_3R)]$ have been reported [28]. Other simple π-complexes are rare. $[(C_5H_5)_2NbCl_2]$ reacts with cyclopropene itself in the presence of sodium to yield a product characterised spectroscopically as $[(C_5H_5)_2Nb(C_3H_4)]$ [29]. A further cyclopropene complex is formed from $[Ir(CO)Cl(PPh_3)_2]$ and 3,3-diphenylcyclopropene [30]. The product, $[Ir(CO)Cl(PPh_3)_2(C_3H_2Ph_2)]$, reacts with a further molecule of $[Ir(CO)Cl(PPh_3)_2]$ to produce a metallacyclobutene complex, $[Ir(CO)Cl(PPh_3)_2(CH{=}CHCPh_2)]$, and such ring opening reactions are, in fact, much more characteristic of metal–cyclopropene chemistry than simple complex formation.

The products, metallacyclobutenes and vinylcarbene complexes, may be regarded as extreme forms of the same species.



It is therefore not surprising that many reactions are known in which metallacyclobutenes and vinylcarbene complexes are produced, even though a cyclopropene complex is often implicated as an intermediate. Further, the ultimate reaction product is dictated not only by the metal complex but also by the cyclopropene. For example, $[Pt(PPh_3)_2(C_2H_4)]$ and C_3F_4 yield not a perfluorocyclopropene adduct but $[Pt(PPh_3)_2(CF{=}CFCF_2)]$ [31]. Similarly, $[Ir(CO)Cl(PR_3)_2]$ (R=Me or Ph) and perfluorocyclopropene give isomeric products $[Ir(PR_3)_2(CO)Cl(CF{=}CFCF_2)]$ [32], both of which have P *trans* P, but one of which has CF *trans* CO and the other of which has CF *trans* Cl. In contrast, $[RuCl_2(PPh_3)_4]$ reacts with 3,3-diphenylcyclopropene to generate the vinylcarbene complex $[RuCl_2(PPh_3)_2(CHCH{=}CPh_2]$ [33].

Early transition elements show more complex behaviour. For example, $[(C_5H_5)_2Ti(PMe_3)_2]$ and 3,3-dimethylcyclopropene react in 1:1 molar ratio to generate $[(C_5H_5)_2Ti(PMe_3)(CHCH{=}CMe_2)]$ [34], but a four-fold excess of the cyclopropene produces not only this material but also a labile complex identified as $[(C_5H_5)_2Ti(PMe_3)(C_3H_2Me_2)]$ which reacts above 0°C with the excess of cyclopropene to yield $[(C_5H_5)Ti(CH{-}CH{-}CH{-}CH)]$.



There is similar zirconocene chemistry.

Polymerisation of cyclopropenes with or without incorporation of other groups, such as CO, is a common observation [35], but since polymeric products are not detected in nitrogenase systems, such reactions will not be discussed further.

The reaction pathway observed is a function of the cyclopropene. $[(C_5H_5)_2Ti(PMe_3)_2]$ and 1,2-diphenylcyclopropene form a 1:1 cyclopropene adduct with the loss of one PMe_3, and the olefin complex $[(C_5H_5)_2Zr(PMe_3)(CH_2{=}CHEt)]$ reacts with the same cyclopropene to lose butene and generate a homologue. Both Ti and Zr complexes can lose the remaining PMe_3 to form $[(C_5H_5)_2M(CHCPh{=}CPh)]$ (M = Ti or Zr) [36]. Both 1,2- and 3,3-diphenylcyclopropene react with $[(C_5H_5)_2Ti(PMe_3)_2]$, apparently to yield metallacyclobutene complexes in both cases. However, the product from the latter cyclopropene alone reacts with the displaced PMe_3 to generate the isolated vinylcarbene complex. The reason for the isolation of the metallacyclobutene complex from 1,2-diphenylcyclopropene is believed to be unfavourable steric interactions in the vinylcarbene complex which would have been produced subsequently. A further, rather unusual, example of cyclopropene–vinylcarbene conversion is that of the reaction of the Fischer carbene $[W(CO)_5(CHC_6H_4R)]$ (R = H or Me) at −80°C to give a cyclopropene complex, $[W(CO)_5(CHCPhC(H)(C_6H_4R)]$, which, in turn, above −40°C, forms $[W(CO)_5(CHCPh{=}C(H)(C_6H_4R)]$. The rearrangement is apparently intramolecular [37].

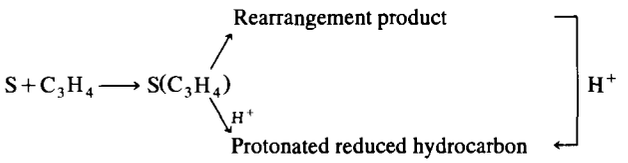
It is not clear, however, whether metallacyclobutenes and vinylcarbene complexes are accessible directly from the cyclopropene complexes, and/or whether they can interconvert directly without the intermediate of a cyclopropene complex. The possibility of an η^3-vinylcarbene, $M{=}CH{-}CH{=}CH_2$ must also be considered. A metallacyclobutene generated from the reaction of $[(C_5H_5)_2TiCH_2AlMe_2]$ and $EtCCCMe{=}CH_2$ in the

presence of base produces three isomeric metallacyclobutenes $[(C_5H_5)_2Ti\{C_3H_2Et(CMe{=}CH_2)\}]$ in equivalent amounts which interconvert rapidly via a substituted vinylcarbene complex [38].

A final example is taken from tungsten chemistry. The complex $[WCl_2(PR_3)_3(NAr)]$ reacts with 3,3-diphenylcyclopropene to lose one PR_3 group and give a cyclopropene complex $[WCl_2(PR_3)_2(NAr)(C_3H_2Ph_2)]$ if the groups R (PR_3 = $P(OMe)_3$ or PMe_2Ph) and Ar (= Ph) are small. This can yield a vinylcarbene complex, for example, upon irradiation. However, for larger R, for example $PR_3 = PEt_2Ph$ and $Ar = C_6H_3Pr^i_2$-2,6, two isomeric vinylcarbene complexes $[WCl_2(Pr_3)_2(NAr)(CHCH{=}CPh_2)]$ are formed directly and the cyclopropene adduct is not observed [39].

The evidence thus seems to suggest that cyclopropenes can form a range of derivatives based upon a

single cyclopropene molecule: cyclopropene complexes, metallacyclobutenes, and vinylcarbene complexes, as well as allene complexes and methylacetylene derivatives produced by isomerisation of cyclopropenes. Any or all of these could explain some of the observations reported of the reduction of cyclopropene by nitrogenases. For example, allene generation prior to protonation could explain the 2,3-deuteration of the product propene generated by nitrogenase. We selected as a model reaction scheme the following sequence, in which S represents an "active site", in a nitrogenase or in a model.



In this scheme, H^+ may come from an external acid or may arise from hydrido-ligands within S. We now summarise our data on a range of models for S.

3.1. Functional models for the active site of nitrogenases

The reduction of cyclopropenes, including cyclopropene itself, by model complexes, yields cyclopropanes and propenes. We investigated [16] two molybdenum hydrides, namely $[MoH_4(dppe)_2]$ and $[MoH_4(PMePh_2)_4]$. Both were reluctant to react at all, either with cyclopropene or 3,3-dimethylcyclopropene, in the absence of added acid, to yield volatile products. However, $HBF_4 \cdot Et_2O$ with C_3H_4 or 3,3-dimethylcyclopropene and a hydrido-complex does react, and the former hydrocarbon produces a high proportion of propene and some of the cyclopropane. The latter hydrocarbon produces a higher relative proportion of the corresponding cyclopropane. Very surprisingly, both hydrides also produce small amounts of C_2H_4 and C_2H_6, suggesting that C–C bond cleavage occurs.

In contrast $[FeH(H_2)(dmpe)_2][BPh_4]$ (dmpe = $Me_2PCH_2CH_2PMe_2$) reacts with either cyclopropene in the absence of extra acid to produce both the cyclopropane and the propene. In none of our experiments did the reactions of hydride and cyclopropene give us solid, characterisable products [16,40].

Parallel reactions of these hydrides with the alkyne isomers of the cyclopropenes, namely propyne and 3-methylbut-1-yne, without $HBF_4 \cdot Et_2O$ in the case of iron, yielded the propene analogues, and no cyclopropanes. Finally, we used 1,1-dimethylallene and allene itself. This time characterisable solids were obtained from the iron system, and from both iron and molybdenum hydrides and allenes and acid we isolated the propylene analogues [16]. Clearly, complexes such as $[Fe(dmpe)_2(H\cdots CH_2\cdots C=CMe_2][BPh_4]$, obtained from $[FeH(H_2)(dmpe)_2]^+$ and 1,1-dimethylallene, would be expected to pick up hydrogen at the central carbon atom $\cdots C=$ upon protonation, and so it proved. Allene itself is reduced by nitrogenase in

Table 3
Products of the reactions of platinum(0) cyclopropene products with HCl and DCl

Novel platinum adducts formed	Products formed on addition of 2 equiv. HCl	Products formed on addition of 2 equiv. DCl
X in $[(PPh_3)_2PtX]$	*cis*-[(PPh_3)2PtCl2] plus:	*cis*-$[(PPh_3)_2PtCl_2]$ plus:
3,3-Diphenylcyclopropene	1,1-diphenylcyclopropane	2,3-d_2-1,1-diphenylcyclopropane
	3,3-diphenylpropene	3,3-d_2-1,1-diphenylpropene
	1,1-diphenylpropene	*cis*-1,3-d_2-3,3-diphenylpropene
	1,2-diphenylpropene	*trans*-1,3-d_2-3,3-diphenylpropene
		3,3-d_2-1,2-diphenylpropene
1,2-Diphenylcyclopropene	*cis*-1,2-diphenylcyclopropane	1,2-d_2-1,2-diphenylcyclopropane
	2,3-diphenylpropene	3,3-d_2-2,3-diphenylpropene
3-Methyl-3-phenylcyclopropene	1-methyl-1-phenylcyclopropane	*cis*- and *trans*-2,3-d_2-1-methyl-1-phenylcyclopropane
	3-phenylbut-1-ene	3,3-d_2-2-phenylbut-1-ene
	2-methyl-3-phenylpropene	*trans*-1,3-d_2-3-phenylbut-1-ene
	2-phenylbut-1-ene	1,1-d_2-2-phenyl-but-2-ene
	trans-2-phenyl-but-2-ene	3,4-d_2-3-phenylbut-1-ene
		3,3-d_2-2-methyl-3-phenylpropene
		cis-1-d-2-(d-methyl)-3-phenylpropene
1,2-Dibutylcyclopropene	indistinguishable by ^{1}H NMR spectroscopy	–
1-Butyl-1-trimethylsilylcyclopropene	indistinguishable by ^{1}H NMR spectroscopy	–
3,3-Dimethylcyclopropene [a]	1,1-dimethylcyclopropane	2,3-d_2-1,1-dimethylcyclopropane
	3-methylbut-1-ene	
	2-methylbut-1-ene	
	2-methylbut-2-ene	
Cyclopropene [a]	cyclopropane > 95%	–

[a] previously prepared by Visser et al. [23].

deuterated water to produce 2,3-dideuteropropene [15], so the reduction of allene is precisely modelled. What this implies for cyclopropene as a substrate for nitrogenase is not clear.

We therefore decided to check the reactivity of a range of platinum(0) cyclopropene complexes with acid, these being the only easily accessible materials which unequivocally contain complexed cyclopropenes essentially unchanged. The results from these experiments are reported in Table 3.

In all the protonations we attempted, the appropriate platinum(II) dichloro-complex formed rapidly and was isolated in quantitative yield. This virtually excludes a mechanism in which the cycloolefin is lost and oxidative addition of HCl to a platinum(0) intermediate ensues. The hydrocarbon products from the triphenylphosphine-containing reactions were generally a mixture of cyclic and ring-opened materials. The notable exception is the cyclopropene complex itself, which yielded cyclopropane and only a trace of what appeared to be propene. In fact, niobium chemistry has yielded a similar observation [29].

There appears to be some steric control on the product, as shown by the example of 1,2-diphenylcyclopropene. However, much more than that is involved. For example, 3,3-diphenylcyclopropene produces 1,1-diphenylcyclopropane and 3,3-diphenylpropene as major products. These could be taken to imply a transition state in which either the original double bond or a carbon–carbon single bond were open to attack by a hydrogen species. The smaller quantities of 1,1-diphenylpropene, could, with some allowance for fantasy, be explained by a similar process. What is quite impossible to explain at present is how the 1,2-diphenylpropene forms. Similar shifts are also observed with methyl groups in the dimethylcyclopropene protonations.

Deuteration experiments also show a certain degree of stereospecificity. Referring again to the case of 3,3-diphenylcyclopropene, deuteration at the 2 and 3 positions of the diphenylcyclopropane would be expected. The 3,3-d_2-1,1-diphenylpropene (and the 3,3-d_2-1,2-diphenylpropene) are consistent with the π-allyl cation type of intermediate suggested by Schrauzer and are not unexpected if one accepts that protic attack at a carbon-carbon single bond of the cyclopropene is likely [41]. Thus *cis*- and *trans*-CHD=CH-CDPh_2 are consistent with observations on C_3H_4 reduction by nitrogenase, and the protonation (rather than the deuteration) experiments cited in Table 3. A more detailed analysis of the material presented in Table 3 requires more experimental data.

4. Preliminary conclusions

In general, the products of protonation of cyclopropenes in the presence of transition metal complexes

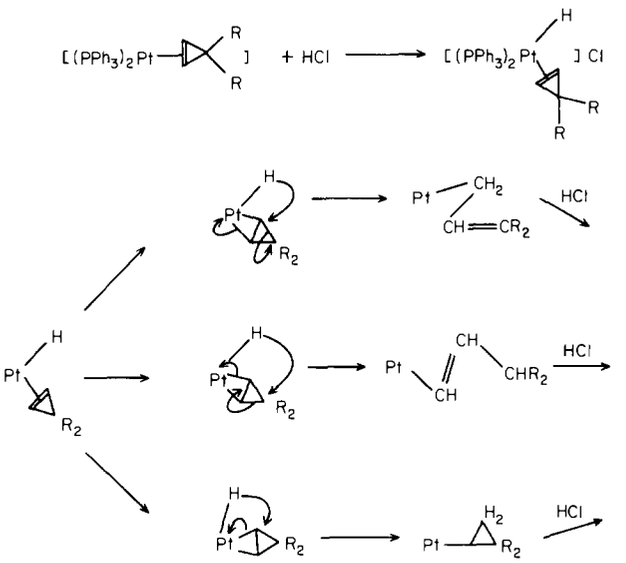


Fig. 2.

are very diverse, and depend not only on the transition metal but also on the acid used and the solvent. This makes the interpretation of nitrogenase chemistry even more difficult. The platinum complexes are a particularly simple case for analysis, but nevertheless seem to provide more reaction pathways than have been observed with nitrogenase. Nevertheless, the evidence certainly suggests that reduction procedes via a complex of cyclopropene, in nitrogenase as in the model system.

There is clearly more than one pathway and we believe that this attack is probably via the metal, as demonstrated for the protonation of acetylene to yield ethylene mediated by molybdenum complexes. Indeed, it must be possible for protons (or hydride) to move from metal to cyclopropene, even if indirectly, because this is what happens with $[FeH(H_2)(dmpe)_2]^+$ and cyclopropene, when cyclopropane and propene are produced without addition of any further acid [15]. We suggest that the tentative scheme in Fig. 2 is in accord with most of the facts, and that this may be the kind of reactivity exhibited by nitrogenase.

Reaction with a further molecule of HCl then generates the observed products. Further work is needed to establish this with certainty.

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