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A New Approach to the Air Oxidation of Alkenes Employing Metal Nitro Complexes as Catalysts

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Alkenes are stoichiometrically and, in the presence of air, catalytically oxidized by *cis*-bis(acetonitrile)chloronitropalladium(II) (1). Oxidation of monosubstituted terminal alkenes and *trans*-cyclooctene yields the corresponding ketone, oxidation of cyclopentene and cyclohexene the corresponding allyl alcohol, and oxidation of bicyclic alkenes the corresponding epoxide, each with good selectivity for the respective product. Other alkenes give varying mixtures of the above products together with, in some cases, the α,β-unsaturated ketone. Vinyl ethers yield the corresponding ester while (trimethylsilyl)ethylene yields (trimethylsilyl)acetaldehyde. The selectivities are rationalized on the basis of ease of β-hydrogen elimination in observed intermediate heterometallacyclopentane complexes 3 formed by nucleophilic attack of the nitro oxygen atom on the coordinated alkene in alkene nitro complexes 2. The general role of metallacycles in metal-mediated alkene oxidations and the advantages and disadvantages of intra- vs. intermolecular metal nitro catalyzed alkene oxidations are discussed.

A major obstacle to the efficient catalytic air epoxidation of alkenes is stoichiometric coproduct formation. In the commercial epoxidation of both ethylene (eq 1)[1] and propylene (eq 2 and 3),[2] only one of the two O_2 oxygen

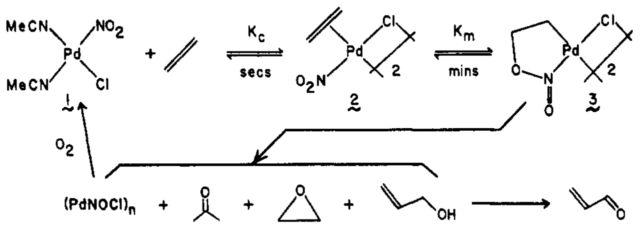
$$^7/_6C_2H_4 + O_2 \xrightarrow{Ag} C_2H_4O + ^1/_3CO_2 + ^1/_3H_2O \qquad (1)$$

$$RH + O_2 \rightarrow RO_2H \qquad (2)$$

$$C_3H_6 + RO_2H \xrightarrow{Mo(VI)} C_3H_6O + ROH \qquad (3)$$

atoms is converted to the desired epoxide. This is a direct consequence of the asymmetric activation of the dioxygen molecule that occurs before or during interaction with the alkene substrate.

Scheme I. Catalytic Alkene Oxidation by $Pd(CH_3CN)_2ClNO_2$



We[3] and others[4] have been attempting to exploit the observation that dioxygen can be *symmetrically* cleaved by certain metal nitrosyl complexes (eq 4).[5] In principle

$$2MNO + O_2 \rightarrow 2MNO_2 \qquad (4)$$

this constitutes a solution to the epoxidation coproduct problem since the oxidizing power of both oxygen atoms of the O_2 molecule becomes stored in equivalent form as two nitro groups. When we began this work, however, there were no clear examples of the necessary subsequent

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(1) (a) Kilty, P. A.; Sachtler, W. M. H. *Cat. Rev.—Sci. Eng.* **1974**, *10*, 1-16. (b) Ayame, A.; Takeno, N.; Kanoh, H. *J. Chem. Soc., Chem. Commun.* **1982**, 617-618.

(2) Landau, R.; Sullivan, G. A.; Brown, D. *Chemtech.* **1979**, *9*, 602-607.

(3) (a) Andrews, M. A.; Kelly, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 2894-2896. (b) Andrews, M. A.; Cheng, C.-W. F. *J. Am. Chem. Soc.* **1982**, *104*, 4268-4270. (c) Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. F.; Kelly, K. P. *J. Am. Chem. Soc.* **1984**, *106*, 5913.

(4) (a) Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am. Chem. Soc.* **1979**, *101*, 270-272. (b) Tovrog, B. S.; Mares, F.; Diamond, S. E. *J. Am. Chem. Soc.* **1980**, *102*, 6616-6618. (c) Tovrog, B. S.; Diamond, S. E.; Mares, F.; Szalkiewicz, A. *J. Am. Chem. Soc.* **1981**, *103*, 3522-3526. (d) Diamond, S. E.; Mares, F.; Szalkiewicz, A.; Muccigrosso, D. A.; Solar, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4266-4268. (e) Muccigrosso, D. A.; Mares, F.; Diamond, S. E.; Solar, J. P. *Inorg. Chem.* **1983**, *22*, 960-965. (f) Tovrog, B. S.; Diamond, S. E.; Mares, F. U.S. Patent 4 191 696, Mar 1980; 4 322 562, Mar 1982. (g) Diamond, S. E.; Mares, F.; Muccigrosso, D. A.; Solar, J. P. U.S. Patent 4 356 311, Oct 1982. (h) Heumann, A.; Chauvet, F.; Waegell, B. *Tetrahedron Lett.* **1982**, *23*, 2767-2768.

(5) (a) Ishiyama, T.; Matsumura, T. *Annu. Rep. Radiat. Cent. Osaka Prefect.* **1970**, *11*, 50-52 (cf. *Chem. Abstr.* **1972**, *76*, 30252). (b) Tamaki, M.; Masuda, I.; Shinra, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 171-174. (c) Clarkson, S. G.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1972**, 670-671; *Inorg. Chem.* **1973**, *12*, 1528-1534. (d) Clark, G. R.; Grundy, K. R.; Roper, W. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Chem. Commun.* **1972**, 119-120. (e) Trogler, W. C.; Marzilli, L. G. *Inorg. Chem.* **1974**, *13*, 1008-1010. (f) Kubota, M.; Phillips, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 5637-5638. (g) Ugo, R.; Bhaduri, S.; Johnson, B. F. G.; Khair, A.; Pickard, A.; Benn-Taarit, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 694-695. (h) Bhaduri, S. A.; Bratt, I.; Johnson, B. F. G.; Khair, A.; Segal, J. A.; Walters, R.; Zuccaro, C. *J. Chem. Soc., Dalton Trans.* **1981**, 234-239.

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Table I. Stoichiometric Oxidations under Nitrogen Employing $Pd(CH_3CN)_2ClNO_2$

						% yield organic products based on Pd[b]				
alkene	[Pd], mM	alkene/Pd	solv[a]	temp, °C	time, h	ketone	epoxide	allyl alcohol	α,β-unsaturated ketone	other(s)
ethylene	15	~2	DM	25	11	57	–	–	–	–
1-butene	20	XCS	DM	25	19	98	–	–	–	3
1-decene	8	1.0	tol	25	24	95	–	–	–	–
1-decene	8	1.0	tol	85	0.5	73	0.9	–	–	–
allylbenzene	19	1.0	DCE	25	18	40	–	–	–	5
styrene	29	1.0	tol	25	19	6	–	–	–	5
cis-2-butene	20	~1	DCF	25	72	36	2,[c] 7[d]	–	–	–
trans-2-butene	20	~1	DCF	25	72	44	2,[c] 9[d]	–	–	–
isobutylene	20	~1	DCF	25	24	–	16	–	–	–
methylenecyclohexane	29	1.0	tol	60	1	–	35	–	–	12
cyclopentene	29	1.0	DCE	25	24	5	5	25	5	5
cyclohexene	29	1.0	DCE	60	2	3	–	34	5	12
4-*t*-butylcyclohexene	29	1.0	DCE	60	4	ND	5	ND	ND	ND
cycloheptene	29	1.0	DCE	25	20	4	21	2	32	8
cycloheptene	29	1.0	DCE	60	2	2	34	9	17	6
cyclohept-2-en-1-ol	29	1.0	DCE	25	24	14	0	12	24	7
cis-cyclooctene	29	1.0	DCE	60	3	6	12	7	–	10
trans-cyclooctene	29	1.0	DCE	25	24	45	–	–	–	10
norbornene	19	1.0	tol	25	120	–	90	–	–	–
bicyclo[2.2.2]oct-2-ene	20	1.0	DCE	60	2	–	70	–	–	–
bicyclo[3.2.1]oct-2-ene	19	1.0	DCE	60	2	–	50	–	–	–

[a] DM = dichloromethane; tol = toluene; DCE = 1,2-dichloroethane; DCF = deuteriochloroform. [b] – = < 2%; ND = not determined. [c] Cis epoxide. [d] Trans epoxide.

O atom transfer from the metal nitro group to the alkene (eq 5, L = alkene).[6] In contrast, related O atom transfers to inorganic substrates such as CO,[7] CS,[8] and NO[9] were well-known.[10]

$$MNO_2 + L \rightarrow MNO + LO \qquad (5)$$

We report here some of the details of our previously communicated findings[3a,b] that demonstrate alkene oxidation, including epoxidation, catalyzed by the palladium nitro complex *cis*-bis(acetonitrile)chloronitropalladium(II) (1). The synthesis and characterization of the catalyst 1 and reaction intermediates 2 and 3 (Scheme I) are discussed elsewhere.[3c] This paper covers the oxidized organic products that result from further reactions of these intermediates. Following our initial communication,[3a] Heumann and co-workers[4h] applied our catalyst to bicyclic alkenes and obtained results similar to a few of those presented here.

In contrast to our monometallic approach to metal nitro catalyzed alkene oxidation, workers at Allied[4a-g] have independently pioneered bimetallic systems. These are based on macrocyclic cobalt nitro complexes and require palladium[4b] or thallium[4d] cocatalysts to effect the oxidation of alkenes. They have also reported a rhodium monometallic system.[4e] Some of the advantages and disadvantages of the two approaches and the possible general role of metallacycles in metal-mediated oxidations are also discussed here.

Results

Stoichiometric Alkene Oxidations with 1. A wide range of alkenes can be stoichiometrically oxidized by nitro complex 1 under mild conditions in nondonor organic solvents (Table I). The primary oxidation products formed are ketones, epoxides, and allyl alcohols. The former two are stable under the reaction conditions, but the latter are sometimes dehydrogenated to give α,β-unsaturated ketones. The selectivities for any one of the primary products can be quite high depending on the alkene employed as substrate. A detailed analysis of the organic product distributions for different classes of alkenes is presented in the Discussion.

The major palladium byproduct in these stoichiometric reactions is usually a brownish black precipitate of the polymeric species $[PdCl(NO)]_n$ (4).[11] This complex was prepared some time ago in what may actually be the first example of an O atom transfer reaction involving a metal nitro complex.[6] In the presence of air and acetonitrile, 4 can be slowly reoxidized to nitro complex 1, thus forming the basis for catalytic oxidation of alkenes by atmospheric oxygen.

Catalytic Alkene Oxidations with 1. Table II lists some examples of catalytic air oxidation of alkenes employing nitro complex 1 and related species. The reaction mixture remains homogeneous at all times (except at elevated temperatures where the solvent vapor substantially lowers the partial pressure of oxygen) despite the fact that the reoxidation of nitrosyl complex 4 is significantly slower than the oxidation of the alkene by nitro complex 1. Apparently a soluble nitrosyl precursor to 4 is more readily oxidized under the reaction conditions than 4 itself.[12]

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(6) The reaction of ethylene with aqueous acidic $PdCl_2$ in the presence of $NaNO_2$ has been reported to give acetaldehyde plus $[Pd(NO)Cl]_n$ (Smidt, J.; Jira, R. *Chem. Ber.* **1960**, *93*, 162–165). It is not known whether this is an O atom transfer reaction of an in situ produced palladium nitro complex or whether it is traditional Pd(II) Wacker chemistry coupled with acidolysis of a palladium nitro complex to a nitrosyl complex. In theory these could be distinguished by an ^{18}O labeling study, but in practice the isotope label in the ketone would probably be washed out by exchange with the acidic aqueous medium.

(7) Booth, G.; Chatt, J. *J. Chem. Soc.* **1962**, 2099–2106.

(8) Efraty, A.; Arneri, R.; Sikora, J. *J. Organomet. Chem.* **1975**, *91*, 65–70.

(9) Ileperuma, O. A.; Feltham, R. D. *J. Am. Chem. Soc.* **1976**, *98*, 6039–6040.

(10) For a comprehensive bibliography of O atom transfer reactions of metal nitro complexes see: Andrews, M. A.; Chang, T. C.-T., Cheng, C.-W. F., *Organometallics*, in press.

(11) Under certain conditions, particularly those involving polar solvents, this complex is converted to a partially characterized black nitrosyl complex (see Experimental Section).

(12) Nitrosyl complex 4 does not react with either alkenes or acetonitrile (~10-fold excess) in inert solvents in the absence of air. It does dissolve in neat acetonitrile to give unstable yellow solutions.

Table II. Catalytic Oxidations in Air Employing $Pd(CH_3CN)_2ClNO_2$

						% yield organic products based on Pd[b]			
alkene	[Pd], mM	alkene/ Pd	solv[a]	temp, °C	time, h	ketone	epoxide	allyl alcohol	α,β-unsaturated ketone
ethylene	8	XCS	DM	25	48	125	–	–	–
propylene	13	XCS	tol	25	48	645	–	–	–
1-decene	7	12	tol	25	24	240	–	–	–
1-decene	8	12	tol	65	1	375	–	–	–
1-decene[c]	7	11	tol	25	48	482	–	–	–
1-decene[d]	7	12	tol	60	3	334	–	–	–
t-butylethylene	4	28	Bz	25	120	1150	–	–	–
n-butyl vinyl ether	8	25	DM	25	50	123	–	–	–
cyclopentene	29	10	DM	25	24	23	15	104	15
cycloheptene	29	10	DCE	60	3	31	137	50	71
norbornene	5	10	EA	60	12	–	690	–	–
norbornene	5	10	DCE	60	5	–	255	–	–

[a] DM = dichloromethane; tol = toluene; Bz = benzene; DCE = 1,2-dichloroethane; EA = ethyl acetate. [b] – = <2%. [c] Using $Pd(CH_3CN)_2BrNO_2$ as catalyst. [d] Using $[Pd(NO)Cl]_n$ as catalyst.

In all cases, the catalyst is short-lived, generally decomposing in less than ten turnovers. Of the reaction variables investigated—concentrations, ratios of alkene to palladium, oxygen pressure, temperature, auxiliary ligands, solvent, and alkene—only the last four had a significant effect on catalyst lifetime. Raising the temperature (entry 4), or even better, changing the auxiliary halide from chloride to bromide (entry 5), noticeably increased the turnover number. Unfortunately, all attempts to prepare iodo(nitrile)palladium complexes appeared to result in the formation of palladium metal and molecular iodine. The dinitro and nitro thiocyanato analogues of 1 are stable but yield significant amounts of 2-nitro-1-decene on reaction with 1-decene.[3a,13] The acetonitrile ligands of 1 can be replaced by other nitriles with little effect on the reaction, but replacement with phosphines or amines or the use of donor solvents kills or markedly inhibits the reaction. Polar, nondonor solvents (e.g., ethyl acetate), on the other hand, sometimes increase catalyst lifetime.

In general, the spent catalyst is ultimately recovered in the form of an allylchloropalladium dimer.[14] It is therefore not surprising that alkenes lacking suitable allylic hydrogens (e.g., *tert*-butylethylene and norbornene) give higher turnovers. In the case of *tert*-butylethylene, a 2-isopropylallyl complex still eventually forms via a palladium-induced carbonium ion rearrangement.[15] In the case of cyclic alkenes, some of the catalyst is converted to Pd metal during dehydrogenation of the product allyl alcohol, while with norbornene, a brown organic containing precipitate forms that probably contains polymeric norbornene.[16] Rapid catalyst deactivation with ethylene, despite the lack of allylic hydrogens, is apparently due to the formation of an unreactive partially characterized black nitrosyl complex.[11] As is necessary for a catalytic cycle based on a nitro–nitrosyl redox couple, the corresponding nitrosyl complex can also be employed as the catalyst (entry 6).

The effect of reaction variables on the product distributions is minimal, especially in comparison to the effect of changing alkenes or the catalyst auxiliary ligands. The only readily apparent trend detected is that increasing the reaction temperature increases the yield of epoxide for both cycloheptene and 1-decene.

Discussion

Catalyst Development. The primary goal of the present work was a demonstration of O atom transfer from a metal nitro complex to an alkene to give an epoxide and a metal nitrosyl. In conjunction with previous literature on the oxidation of metal nitrosyls to metal nitro complexes,[5] this would then constitute a formal solution to the coproduct problem in catalytic alkene epoxidation. Our initial efforts were directed toward reactions of d^8 nitro phosphine complexes with alkenes since these complexes were known to oxidize CO to CO_2.[7,17] Of the complexes investigated—$Ni(PBu_3)_2(NO_2)_2$, $Pd(PBu_3)_2(NO_2)_2$, $Pd(PPh_3)_2ClNO_2$, $[Pt(PBu_3)ClNO_2]_2$, $[Pd(PBu_3)ClNO_2]_2$, and $Rh(PPh_3)_3NO$ (in air)—only the last two oxidized 1-decene and these gave only about a 10% yield of 2-decanone. Compared to CO, alkenes are generally poorer ligands and are less easily oxidized. This suggests that phosphines are undesirable as auxiliary ligands in a metal nitro mediated alkene oxidation system for three reasons: phosphines are (1) bulky ligands (inhibiting associative alkene coordination), (2) strong ligands (inhibiting phosphine displacement by alkene), and (3) easily oxidizable ligands (limiting catalyst lifetimes).

We have found that nitriles are ideal auxiliary ligands for the present purposes, being small, labile, and relatively nonoxidizable. A catalyst derived from the well-known bis(nitrile)dichloropalladium complexes seemed particularly attractive in view of the long recognized ability of such species to form alkene complexes.[18] This led to a simple

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[13] Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. F.; Kapustay, L. V.; Kelly, K. P.; Zwiefel, M. J. *Organometallics* **1984**, *3*, 1479.

[14] The mechanism by which these allyl complexes form is not yet clear but does *not* seem to be a simple allylic deprotonation in alkene complex 2 accompanied by loss of HNO_2. Stoichiometric oxidation of 1-decene by 1 gives a >95% yield of 2-decanone, yet the catalytic reaction under the same conditions yields only 2.4 turnovers, hence catalyst deactivation must follow the O atom transfer reaction. One possibility is (cf. ref 6 and Bhaduri, S. A.; Bratt, I.; Johnson, B. F. G.; Khair, A.; Segal, J. A.; Walters, R.; Zuccaro, C. *J. Chem. Soc., Dalton Trans.* **1981**, 234–239, and Dubrawski, J.; Kriege-Simondsen, J. C.; Feltham, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 2089–2091):

$$2Pd(NO)Cl + 3\ CH_2{=}CHCH_2R \rightarrow [Pd(CH_2CHCHR)Cl]_2 + N_2O + CH_3COCH_2R + H_2$$

[15] Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627–4629. (b) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1981**, *20*, 4036–4038.

[16] Kiseleva, N. V.; Varshavskii, Yu. S.; Buzina, N. A.; Kormer, V. A. *Dokl. Akad. Nauk SSSR* **1974**, *217*, 348–351.

[17] (a) Doughty, D. T.; Gordon, G.; Stewart, R. P., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2645–2648. Feltham, R. D.; Kriege, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5064–5065. (c) Kriege-Simondsen, J.; Elbaze, G.; Dartiguenave, M.; Feltham, R. D.; Dartiguenave, Y. *Inorg. Chem.* **1982**, *21*, 230–236. (d) Kriege-Simondsen, J.; Bailey, T. D.; Feltham, R. D. *Inorg. Chem.* **1983**, *22*, 3318–3323. (e) Doughty, D. T.; Stewart, R. P., Jr.; Gordon, G. *J. Am. Chem. Soc.* **1981**, *103*, 3388–3395.

[18] Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882–884.

Table III. Predicted Behaviors in Nitrosooxymetalation of Alkenes by Metal Nitro Complexes

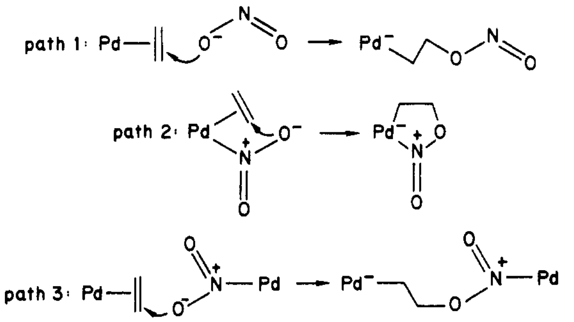
	intramolecular mechanism			intermolecular mechanisms		
	stereochemistry			stereochemistry		
alkene	addition	substitution	product	addition	substitution	product
simple	cis	undefined	ketone	trans	undefined	ketone
cis-cycloalkene	cis	cis	epoxide	trans	trans	ketone
trans-cyclooctene	cis	trans	ketone	cis (or no rxn)	trans (or no rxn)	ketone (or no rxn)
bicyclic	cis	cis	epoxide	cis (or trans)	cis (or trans)	epoxide (or ketone)

preparation of the new nitro complex *cis*-Pd$(CH_3CN)_2ClNO_2$ (1).[3c] The acetonitrile complexes offer several advantages over analogous benzonitrile complexes. Catalyst preparation and product isolation are simpler due to the solubility of the silver nitrite nitrating reagent in acetonitrile and to the lower boiling point of acetonitrile. In addition, the methyl group of the acetonitrile ligands provides a better NMR probe than the benzonitrile aromatic protons and can be conveniently deuterated if desired. The only disadvantages appear to be the slightly greater ligating strength for acetonitrile vs. benzonitrile and a somewhat lower solubility for the acetonitrile complexes.

Nitro complex 1 proved to be a successful catalyst for the oxidation of a wide variety of alkenes, albeit with low turnovers and selectivities for epoxide (Tables I and II). This demonstrates in principle the feasibility of the metal nitro approach to catalytic alkene epoxidation. This new approach has also been independently developed and confirmed by workers at Allied.[4] In particular, these results show that *kinetic paths exist for O atom transfer from metal nitro groups to alkenes and that the metal nitro group retains sufficient thermodynamic oxidizing strength to effect epoxidation of simple alkenes.* The poor selectivities and low turnovers obtained are disappointing from a practical stand point but have provided a wealth of mechanistic insight, including the principles needed for catalyst improvement.

Reaction Mechanism. The reaction of 1-decene with ^{18}O-labeled 1 yields equally ^{18}O-enriched 2-decanone (see Experimental Section). GC-MS studies show that the trace of 1,2-epoxydecane produced is also ^{18}O labeled. *These alkene oxidations therefore proceed by O atom transfer from the nitro group, not by Pd(II) Wacker chemistry[19] resulting from adventitious water or by free radical autoxidation by traces of air.* In addition control experiments show that bis(nitrile)dichloropalladium(II) complexes are *not* efficient Wacker catalysts for the oxidation of 1-decene in ethyl acetate or acetone containing up to 10 equiv of water.[13]

The clean formation of ketones from terminal alkenes observed and the unlikelyhood of one-electron redox reactions for Pd(II)[20] indicate that O atom transfer from the nitro group to the alkene occurs by a heterolytic two-electron process, not by a radical chain reaction[21] or by an electron-transfer reaction.[22] On the basis of the well-known oxypalladation of alkenes,[23] the most reasonable mechanism for the O atom transfer would be a nucleophilic attack of the nitro oxygen atom on the more highly substituted carbon of the coordinated alkene.[24] This could conceivably take place by one of three paths: (1) attack by a dissociated nitrite ion, (2) internal cyclization of alkene nitro complex 2 to give metallacycle 3, or (3) bimolecular coupling of 2. Path 1 is unlikely since free nitrite ion appears to act as a nitrogen-centered nucleophile toward Pd(II) alkene complexes, leading to the formation of nitroalkenes.[13] Mechanisms analogous to both paths 2 and 3 have been proposed for O-atom transfer from nitro groups to carbon monoxide.[9,17] A path 3 type mechanism has also been proposed for the bimetallic nitro group O atom transfer systems reported by Mares and co-workers.[4b,d]



While the observation of metallacycles 3 under the reaction conditions is circumstantial evidence for path 2, many cases are known in catalytic reactions where the observed intermediates are merely the result of dead-end side equilibria. The high kinetic lability of Pd(II)[3c] unfortunately precludes the use of isotope double labeling experiments[17e] to distinguish between paths 1–3. Differentiation by kinetic rate law is also problematical due to the multiple rapid preequilibria present.[3c] In particular, a comparison of rate data for the in situ stoichiometric reaction and decomposition of isolated metallacycles 3 offers no useful information due to the rapid equilibration of complexes 2 and 3 under the reaction conditions.[3c] The best evidence that we have been able to obtain regarding the mechanism of this reaction is found in the marked stereospecificity seen in the oxidation of cyclic alkenes by nitro complex 1.

For ordinary alkenes and simple *cis*-cycloalkenes, dissociative ionic (path 1) and intermolecular (path 3) ni-

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[19] Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Ruttinger, R.; Kojer, H. *Angew. Chem.* **1959**, *71*, 176–182.

[20] Balch, A. L. *Comments Inorg. Chem.* **1984**, *3*, 51–67.

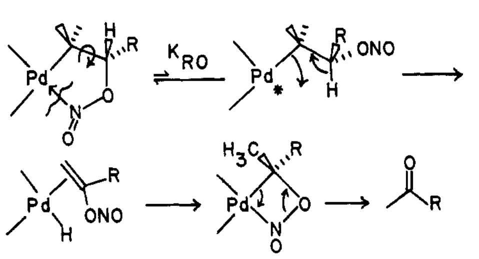
[21] Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981; pp 271–273.

[22] The catalytic oxidations conducted in the presence of air might conceivably involve a different mechanism than the stoichiometric reactions. For example, reoxidation of the product nitrosyl is proposed to involve a peroxy nitrite intermediate MN(=O)OO,[5c,g] which might be expected to react with an alkene to give oxidized products more rapidly than with another nitrosyl species to regenerate the starting nitro complex. The similar product distributions observed for the stoichiometric and catalytic reactions, however, strongly support a uniform reaction mechanism for both processes.

[23] Bäckvall, J.-E. *Acc. Chem. Res.* **1983**, *16*, 335–342 and references therein. Bäckvall, J.-E.; Björkman, E. E.; Pettersson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1984**, *106*, 4369–4373.

[24] Oxypalladation reactions appear to occur by external trans nucleophilic addition of the oxy anion to a slipped alkene complex. The regioselectivity in this case is determined by the stability of the pseudocarbonium ion. (See ref 15 and 23, and Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308–4320. Chang, T. C.-T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361–7362. Wright, L. L.; Wing, R. M.; Rettig, M. F. *J. Am. Chem. Soc.* **1982**, *104*, 610–612.

Scheme II. Proposed Mechanism for Ketone Formation

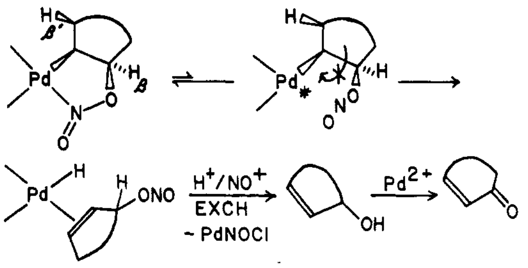


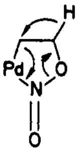
trosooxymetalation of an alkene should proceed via trans addition,[23,24] while intramolecular (path 2) nitrosooxymetalation would almost certainly occur by a cis addition (and does in the one case for which a crystal structure determination is available[3c]). The stereochemistry of intermolecular addition to *trans*-cyclooctene would not be expected to follow these rules, however. Trans addition to *trans*-cyclooctene is impossible due to the steric blocking of one side of the double bond by the aliphatic ring; therefore, intermolecular addition must either proceed with a cis stereochemistry or not occur at all.[25] From these predictions, summarized in Table III, it can be seen that intramolecular path 2 nitrosooxymetalation of *cis*- and *trans*-cyclooctene should be stereospecific, while path 1 or path 3 intermolecular nitrosooxymetalation of the same alkenes would at best only be expected to be stereoselective. The high stereospecificity actually observed in the oxidation of *cis*- and *trans*-cyclooctene by nitro complex **1** (Table I) is therefore strong evidence in favor of intramolecular path 2 and the actual participation of metallacycles **3** in the product-forming sequence. It can also be shown (vide infra) that the specific products formed (epoxide and ketone, respectively) are consistent with intramolecular path 2 and inconsistent with intermolecular paths 1 and 3.[26]

Product Analyses. 1. Monosubstituted Alkenes. Terminal, monoalkyl-substituted alkenes react with nitro complex **1** to give the corresponding methyl ketones (or acetaldehyde in the case of ethylene) in high yields and excellent selectivities (Tables I and II). Metallacycles **3** are readily detected when the reaction is conducted at room temperature and have half-lives of an hour or two.[3c] The relative stability of heterometallacyclic intermediates **3** has precedent in other azapalladacyclopentanes but is in marked contrast with most open-chain palladium alkyls that generally undergo very facile β-hydrogen elimination reactions.[27] This behavior is analogous to that of carbametallacyclopentanes that are orders of magnitude more stable than corresponding open-chain alkyl complexes.[28] The factors responsible for the inhibition of β-hydrogen elimination in metallacycles are not fully understood, but the inability of metallacyclopentanes to achieve a 0° M–C–C–H dihedral angle appears to be a primary factor.[28,29]

In this regard, product formation by the path 3 intermolecular coupling of two molecules of alkene nitro complex **2** (which are in rapid equilibrium with **3**) would appear plausible since decomposition of the intermediate open-chain alkyl complex would be facile due to the lack of dihedral angle constraints. Having tentatively ruled this mechanism out on the basis of stereochemical considerations (vide supra), it becomes necessary to look for alternative possibilities. Heterometallacycles have an additional reaction path open to them that is not available to their carbocyclic analogues, namely, heterolytic ring opening (K_{RO}, Scheme II).[30] β-Hydrogen elimination should be greatly facilitated in such a ring-opened species both by the coordinative unsaturation generated[28a,31] and by the rotational flexibility present permitting attainment of a 0° M–C–C–H dihedral angle. A reasonable pathway, therefore, for the conversion of heterometallacycles **3** to methyl ketones is given in Scheme II. The conversion of the proposed vinyl nitrite intermediate to methyl ketone may occur either by reverse alkene insertion (net ring contraction[32]) and subsequent cleavage (Scheme II) or by a direct proton–nitrosonium ion exchange[33] followed by enol–keto tautomerism (cf. Scheme III). The high selectivities for methyl ketones over isomeric aldehydes is consistent with the absence of detectable concentrations of metallacyclic intermediates **3** substituted on the α-carbon.[3c] An alternative, but we believe far less likely, mechanism for the conversion of metallacycles **3** to ketones would be a concerted retrocyclization coupled with a 1,2-hydride migration (i).

Scheme III. Proposed Mechanism for Allyl Alcohol Formation





i

2. Disubstituted Linear Alkenes. Both *cis*- and *trans*-2-butene give rise to essentially identical product distributions composed mainly of 2-butanone together with small amounts of both the *trans*- and *cis*-epoxides. The metallacyclic intermediates derived from internal alkenes (which are not detectable due to unfavorable equilibria[3c]) could decompose either by intrametallacyclic β-hydrogen elimination to give ketones (Scheme II) or by exometallacyclic β'-hydrogen elimination to give allyl alcohols (cf. Scheme III). In theory β'-elimination ought to occur much more readily than β-elimination since (with noncyclic alkenes) the exometallacyclic alkyl group is free to rotate

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[25] Traylor, T. G. *Acc. Chem. Res.* **1969**, *2*, 152–160.

[26] An attempt[10] has been made to experimentally verify that intermolecular path 3 is in fact not stereospecific and leads to different products than path 2 by employing a bimetallic metal nitro catalyst system.[4b] The results were inconclusive due to ambiguities concerning the exact nature of the active metal nitro catalyst present.

[27] Weinberg, E. L.; Hunter, B. K.; Baird, M. C. *J. Organomet. Chem.* **1982**, *240*, 95–102.

[28] (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528. (b) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529–6536.

[29] Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079–2090.

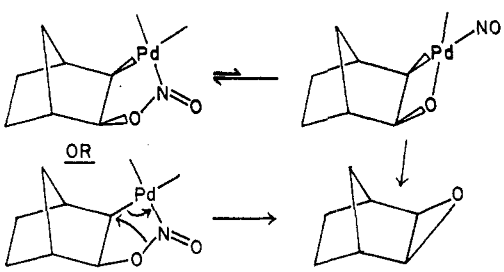
[30] While we have not been able to detect ring-opened isomers of **3**, even in the presence of donor ligands,[3c] the Pd–N bond in **3** must be relatively weak since alkyl nitrites do not displace the labile acetonitrile ligands in $Pd(CH_3CN)_2Cl_2$. The only factor inhibiting ring opening would seem to be the chelate effect.

[31] Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789–2794.

[32] (a) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451–5453. (b) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500–6501.

[33] Caulton, K. G. *Coord. Chem. Rev.* **1975**, *14*, 317–355.

Scheme IV. Proposed Mechanism for Epoxide Formation



allowing attainment of a 0° M–C–C–H dihedral angle. This is apparently a necessary but not sufficient condition for β-hydrogen elimination, however, since α-methyl metallacyclopentanes have been found to be nearly as stable as their unsubstituted analogues.[28] This may be due to unfavorable ring strain effects in the chelated alkene complex that would result from β'-hydrogen elimination. The observation of ketone formation in the present system could be taken as evidence that β-elimination is favored over β'-elimination, perhaps due to electronic substituent effects. More likely explanations we believe are either (a) that initially formed allyl alcohols are isomerized under the reaction conditions to the ketone (a possibility substantiated by control experiments) or (b) that the internal alkene is isomerized to the terminal alkene which then undergoes conversion to the methyl ketone. Palladium(II) is a known alkene isomerization catalyst,[15] and the interconversion of *cis*- and *trans*-2-butene under the reaction conditions is readily demonstrated. 1-Butene could not be detected but would be expected to be present in low equilibrium concentration and would also be more readily oxidized than the internal alkenes as shown by the relative rates of product formation for terminal vs. internal alkenes. Interconversion of the two stereoisomers of 2-butene also accounts for the identical product distributions observed. Alkene isomerization was not generally observed with terminal alkenes due to the more rapid rate of oxidation.

The reaction of 1,1-disubstituted alkenes with nitro complex 1 initially proceeds as for monosubstituted alkenes, giving β,β-disubstituted metallacycles in roughly 50% equilibrium yield.[3c] The absence of β-hydrogen atoms, however, forces a change in the product formation pathways, resulting primarily in epoxide formation and/or π-allyl complex formation. Epoxide formation may proceed by either a concerted fragmentation reaction or by a migratory ring contraction/reductive elimination[34] sequence (cf. Scheme IV).

3. Bicyclic Alkenes. Bicyclic alkenes react with nitro complex 1 to give isolable metallacycles[3c] that slowly decompose with very high selectivities to the corresponding epoxides (Scheme IV). The allylic bridgeheads preclude β'-elimination and γ-elimination (π-allyl complex formation) while β-elimination is severely hampered by the conformational rigidity of the bicyclic skeleton. Thus even in ring-opened isomers of 3, attainment of a 0° Pd–C–C–H dihedral angle is virtually impossible. Similar observations have been made by Heumann and co-workers,[4h] who have studied the reactions of nitro complex 1 with various norbornenes. Their results also demonstrate the regioselectivity of 1 in the oxidation of compounds containing more than one type of double bond.

4. Monocyclic Alkenes. Monocyclic alkenes react with nitro complex 1 to give a wide variety of products whose distributions are markedly dependent upon the ring size and stereochemistry. As is the case for internal linear alkenes, no metallacyclic intermediates are detectable because of unfavorable equilibria.[3c] The observed product distributions, however, clearly implicate metallacycles 3 (path 2) as the key intermediates. If product formation instead took place by path 1 or path 3 intermolecular trans nitrosooxypalladation of a *cis*-cycloalkene, the trans stereochemistry of the intermediate substituted cycloalkane (Table III) would be opposite that shown in Scheme III allowing ready access to conformations with a 0° Pd–C–C–H dihedral angle. This would be expected to result in cycloalkanone formation. In fact, small ring cycloalkenes predominately yield allyl alcohols while large ring *cis*-cycloalkenes give epoxides as the major product.

In the cis-substituted metallacycles derived from the small C_5 and C_6 cycloalkenes, β-hydrogen elimination is difficult, since even in ring-opened isomers of 3 (Scheme III), it is very difficult to achieve a 0° Pd–C–C(ONO)–H dihedral angle. Conversely, the relatively facile attainment of eclipsed ring conformers (0° Pd–C–C–$H_{\beta'}$ dihedral angle) facilitates β'-hydrogen elimination and the observed predominant formation of allyl alcohols. The more conformationally locked alkene 4-*tert*-butylcyclohexene was investigated to see whether both β- and β'-hydrogen elimination would be inhibited. The observation of a small amount of epoxide in this case (vs. none for cyclohexene) is consistent with this, but the effect is minimal. In the larger C_7 and cis-C_8 ring systems, the conformational flexibility is intermediate between that of small-ring and open-chain alkenes leading to mixed product distributions. The origin of the moderately high selectivity for epoxide formation is not clear but may have to do with the relative stabilities of different sized fused-ring systems. This in turn would affect the ring-opening equilibrium, K_{RO}, and the subsequent ease of β-hydrogen elimination.[35] The α,β-unsaturated ketones and a portion of the saturated ketones observed are almost certainly secondary products derived from reactions of the initially formed allyl alcohols (cf. reaction of cyclohept-2-en-1-ol with nitro complex 1 (Table I) and the dehydrogenation of allyl alcohols by Pd(II)).[36]

In marked contrast to the *cis*-cycloalkenes, *trans*-cyclooctene reacts with nitro complex 1 to give almost exclusive formation of cyclooctanone. In this case the fused-ring metallabicycle formed by cis nitrosooxypalladation (path 2) possess the same trans substitution that would result from trans intermolecular addition to a *cis*-cycloalkene (path 1 or 3) and therefore to ketone formation due to the inherent 0° Pd–C–C–H dihedral angle present.

5. Functionalized Alkenes. A brief screening of functionalized alkenes suggests that electron-deficient alkenes are inert toward oxidation by nitro complex 1, while electron-rich alkenes can be successfully oxidized. NMR studies[3c] show that electron-deficient alkenes do not coordinate to either $Pd(CH_3CN)_2Cl_2$ or $Pd(CH_3CN)_2ClNO_2$ (methyl acrylate) or coordinate via the functional group (acrylonitrile). Electron-rich vinyl ethers, however, are known to coordinate to Pd(II)[37] and are readily oxidized by 1 to the corresponding ester (Table II), but alkene oligomerization also seems to occur. Styrene is oxidized to acetophenone in only low yield (NMR spectra of the

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[34] Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120–3128.

[35] Cf. the stability of other metallabicycles toward β-hydrogen elimination: McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 1315–1317.

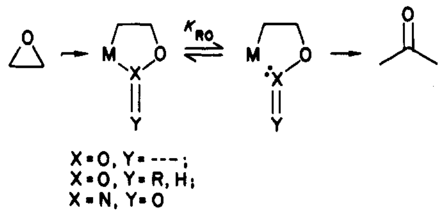
[36] Zaw, K.; Lautens, M.; Henry, P. M. *Organometallics* **1983**, *2*, 197–199.

[37] Wakatsuki, Y.; Nozakura, S.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3426–3429.

reaction mixture show ~50 little peaks from 2.5 to 5.5 ppm). (Trimethylsilyl)ethylene is unique in its reaction with nitro complex 1 in that (trimethylsilyl)acetaldehyde could be detected spectroscopically. This would require reaction via an α-substituted metallacycle, probably resulting from the ability of silyl groups to stabilize β-carbonium ions[24,38] vs. the stabilization of α-carbonium ions by alkyl- and electron-donating substituents.

Role of Metallacycles in Metal-Catalyzed Oxidations. Carbametallacyclobutanes and metallacyclopentanes are firmly established reaction intermediates in a wide variety of metal-catalyzed reactions of hydrocarbons such as alkene metathesis and alkene dimerization.[35,39] In contrast, the participation of heterometallacycles in metal-mediated transformations has not been generally established despite widespread and long standing proposals to that effect, especially in the area of nonradical alkene oxidation.[40] Demonstration of their involvement in the present case raises the question of what role, if any, do these species have in other systems.

A surprisingly large body of literature can be explained by invoking metallacyclic intermediates in combination with the hypothesis that metallacyclic ring opening is a major controlling factor in the determination of product distributions (eq 6). Metallacycles that have undergone ring opening should in general be susceptible to facile β-hydrogen elimination and hence favor ketone and/or allyl alcohol formation (Schemes II and III). Conversely, ring-closed metallacycles should be inhibited toward β-hydrogen elimination and therefore preferentially undergo other reactions such as epoxidation (Scheme IV) or fragmentation. The partitioning between these paths would be primarily determined by the equilibrium constant for heterolytic ring opening (K_{RO}) that is in turn controlled by the chelated metal–heteroatom bond strength. For example, group 8 metal–oxygen bonds are very weak, and therefore these metals primarily catalyze the oxidation of alkenes to ketones,[40,41] while early high-valent d^0 metals have strong metal–oxygen bonds and lead to epoxides with high selectivities.[40,42] The palladium nitro system reported here is intermediate between these extremes as might be expected from the greater ligating strength of nitrogen vs. oxygen donors toward Pd(II). Group 8 dioxygen complexes also provide examples of intermediate cases since ring opening in these systems requires heterolytic cleavage of a covalent metal–oxygen bond as opposed to cleavage of coordinate–covalent bonds in metallacycles derived from alkyl peroxides. In general it is found that group 8 systems that are presumed to oxidize alkenes via dioxygen complexes give rise to higher percentages of non-ketone products[40q,r,41c] than do systems based on alkyl peroxides[40i,j,m] or on dioxygen systems where protons are present[40h,q,r,41a] that can catalyze ring-opening reactions by converting dioxygen complexes into hydroperoxide complexes.[40k,l]



(6)

In view of the tremendous variety of reactions available to transition metal complexes, the tidy generalizations of the last paragraph are certainly an oversimplification of reality. Other mechanisms[40c,e,41b,42,43] can be invoked to explain the varied product distributions observed as a function of metal. In particular, a reasonable hypothesis is that while group 8 metals may sometimes react via metallacycles, high-valent d^0 metals probably usually oxidize alkenes via one or more of the various related mechanisms that postulate attack by the alkene on an electrophilic oxygen.[42c,44,45] It does not seem likely that these questions will be easily resolved; however, since in contrast to the palladium nitro system reported here, reaction intermediates cannot be observed.

Catalyst Modification. Our closing comments concern the prospects for an improved epoxidation catalyst based on a metal nitro complex and the relative merits of the intra- vs. intermolecular approaches. Despite the poor selectivities for epoxide observed in the present system, the observation of epoxide formation in the case of both 1-decene (0.8%) and cycloheptene (35%) shows that the transition state leading to epoxide formation is only a few kilocalories/mole higher than that leading to β-hydrogen elimination. It should be possible to find metal and/or ligand systems where the metal–nitrogen bond strength is sufficiently higher to reverse the selectivities and obtain

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(38) Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153–207.

(39) (a) Puddephatt, R. J. *Comments Inorg. Chem.* **1982**, *2*, 69–95. (b) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491–7496 and references therein. (c) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7416–7418.

(40) (a) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734–750. (b) Mimoun, H. *J. Mol. Catal.* **1980**, *7*, 1–29. (c) Lyons, J. in "Aspects of Homogeneous Catalysis", 1977, *3*, 1–136. (d) Sobczak, J.; Ziolkowski, J. J. *J. Mol. Catal.* **1981**, *13*, 11–42. (e) DiFuria, F.; Modena, G. *Pure Appl. Chem.* **1982**, *54*, 1853–1866. (f) Mimoun, H.; Seree de Roch, I.; Sajus, L. *Tetrahedron* **1970**, *26*, 37–50. (g) Igersheim, F.; Mimoun, H. *J. Chem. Soc., Chem. Commun.* **1978**, 559–560. (h) Mimoun, H.; Perez Machirant, M. M.; Seree de Roch, I. *J. Am. Chem. Soc.* **1978**, *100*, 5437–5444. (i) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047–1053. (j) Roussel, M.; Mimoun, H. *J. Org. Chem.* **1980**, *45*, 5387–5390. (k) Igersheim, F.; Mimoun, H. *Nouveau J. Chim.* **1980**, *4*, 711–713. (l) Igersheim, F.; Mimoun, H. *Nouv. J. Chim.* **1980**, *4*, 161–166. (m) Bregeault, J.-M.; Mimoun, H. *Nouv. J. Chim.* **1981**, *5*, 287–289. (n) Arakawa, H.; Moro-Oka, Y.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2958–2961. (o) Jacobson, S. E.; Tang, R.; Mares, F. *J. Chem. Soc., Chem. Commun.* **1978**, 888–889. (p) Tang, R.; Mares, F.; Neary, N.; Smith, D. E. *J. Chem. Soc., Chem. Commun.* **1979**, 274–275. (q) Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 883–888. (r) Read, G. *J. Mol. Catal.* **1978**, *4*, 83–84. (s) Purcell, K. F. *J. Organomet. Chem.* **1983**, *252*, 181–185. (t) Sheldon, R. A.; Van Doorn, J. A. *J. Organomet. Chem.* **1975**, *94*, 115–129. (u) Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5832–5839. (v) Halfpenny, J.; Small, R. W. H. *J. Chem. Soc., Chem. Commun.* **1979**, 879–880. (w) Broadhurst, M. J.; Brown, J. M.; John, R. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 47–48.

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(42) (a) Sheldon, R. A. *J. Mol. Catal.* **1980**, *7*, 107–126. (b) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* **1976**, *25*, 272–413. (c) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63–74.

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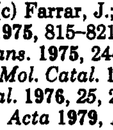
(44) Mihelich, E. D.; Daniels, K.; Eickhoff, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 7690–7692.

(45) We would propose, however, a modification in which the geometry about the vanadium is square pyramidal (**a**) (rather than trigonal bipyramidal[42c] or tetrahedral[44]) since this is the normal geometry for five-coordinate d^0 monooxo complexes; see, for example: Gourdon, A.; Jeannin, Y. *Acta Crystallogr., Sect. B* **1980**, *36B*, 304–309. Bidentate coordination of an alkylperoxide ligand has recently been observed.[43c]



a

high yields of epoxide. This constitutes one of the primary advantages of the intramolecular approach demonstrated here since the intervention of metallacyclic intermediates provides an inherent deterent toward undesirable β-hydrogen elimination. A monometallic system, however, places significant constraints on the choice of catalyst since one metal must be capable of both activating the alkene and supporting a nitro–nitrosyl redox cycle. The bimetallic approach[4b,d] provides greater flexibility in this regard but at the price of a lower effective nucleophilicity of the nitro oxygen toward the alkene (due to absence of the chelate effect) and the loss of built-in inhibition of β-hydrogen elimination provided by a metallacyclic intermediate. Although a practical epoxidation catalyst based on a metal nitro–nitrosyl redox couple has yet to be found, the principle has been established experimentally and some guidelines for future development have emerged.

Experimental Section

General Data. Reactions mixtures were analyzed by using a Perkin-Elmer Sigma 3B gas chromatograph equipped with $^1/_8$ in. × 6 ft stainless-steel columns and a flame ionization detector linked to a Sigma 10B data station which performed electronic integrations. Columns were packed with either A, 15% Carbowax 20M on 80/100 mesh non-acid washed (NAW) Chromosorb W, B, 15% Carbowax 20M on 80/100 mesh AW, dimethylchlorosilanized (DMCS) Chromosorb W, C, 10% OV-210 on 80/100 mesh AW-DMCS Chromosorb P, or D, 10% OV-210 on 80/100 mesh AW-DMCS Chromosorb W. Product yields were determined by using straight-chain hydrocarbons as internal standards. Detector response factors were calibrated by using stock solutions of authentic samples at concentrations similar to those encountered in the oxidation reactions (though a test with the cyclooctene series oxygenates showed no significant concentration dependence in the observed response factors). The cumulative errors resulting from response factor calibration, base line treatment, purity of standards, etc. are believed to be 10–15% or less in most cases. At early reaction times it was usually necessary to quench the reactions with triethylamine, triphenylphosphine, or bis(diphenylphosphino)ethane prior to injection into the GC in order to obtain accurate product yields due to reactions in the hot injection port. Solutions containing only alkene complexes did not form oxidized products in the injection port, but solutions of metallacycles did unless quenched. The validity of the quenching procedure was tested by ^{1}H NMR and by comparing GC yields with IR yields for a 1-decene oxidation. For completed reactions, quenched and unquenched samples gave essentially identical yields except in the case of some of the cyclic alkenes for which quenched samples gave slightly higher yields of allyl alcohol than the unquenched samples. Reported yields in those cases are for the quenched samples.

Infrared spectra were recorded on a Nicolet MX-1 Fourier transform spectrometer. NMR spectra were recorded on a JEOL MH-100 100-MHz or a Varian CFT-20 Fourier transform spectrometer equipped with a dual ^{1}H/^{13}C probe to do ^{1}H NMR at 80 MHz using Me_4Si as internal standard.

Reagent grade solvents were dried over molecular sieves and distilled only if necessary to remove impurities that interferred with the GC integrations. Stoichiometric reactions were conducted under nitrogen using Schlenk techniques and deaerated solvents. Catalytic reactions were conducted in round-bottom flasks exposed to air via a drying tube. Alkenes were normally used as obtained from commercial sources. (Care must be used in this case, especially in reactions employing a large excess of alkene, since trace amounts of alkene autoxidation products present can distort product yields.) *trans*-Cyclooctene[46] and 4-*tert*-butylcyclohexene[47] were prepared as described in the literature. Authentic samples of oxidation products employed as GC standards were commercial samples (except for epoxides that were prepared from the alkene and *m*-chloroperbenzoic acid[48a]) unless otherwise indicated.

Ethylene: GC column A at 60–120 °C. Acetaldehyde formation confirmed by ^{1}H NMR. Catalytic oxidation of ethylene was conducted by placing $Pd(CH_3CN)_2ClNO_2$ (41.4 mg) in a 300-mL three-neck flask, evacuating, and back-filling with 200 torr of ethylene and 560 torr of oxygen. The flask was cooled to −78 °C, and dry dichloromethane (20 mL) and undecane (11.2 mg) were added. The solution was allowed to warm to room temperature, and aliquots were withdrawn periodically for GC analysis.

Propylene. Product analysis was done by quantitative infrared spectroscopy using integrated intensities of the C=O stretch of the product acetone. At the end of a catalytic reaction, the yellow solution was filtered to remove small amounts of black solid and the solvent removed from the filtrate to yield the allyl chloro dimer $[Pd(C_3H_5)Cl]_2$ (90% before chromatography), identified by comparison of IR and ^{1}H NMR spectra (($CDCl_3$) δ 5.50 (1 H, m), 4.12 (2 H, d, J = 6.4 Hz), 3.06 (2 H, d, J = 12.7 Hz)) with those of an authentic sample.

Butenes: GC column B at 60–105 °C. Formation of 2-butanone and isobutylene epoxide were confirmed by ^{1}H NMR and *cis*- and *trans*-2-butene epoxide by coinjection on columns B and D. Alkene isomerization in the case of *cis*- and *trans*-2-butene was monitored by quenching with *m*-chloroperbenzoic acid and determining the ratios of the resulting stereospecifically formed epoxides. In the case of isobutylene, ^{1}H NMR studies of the reaction with 1 showed that (2-methylallyl)chloropalladium dimer (^{1}H NMR ($CDCl_3$) δ 4.04 (2 H, s), 3.04 (2 H, s), 2.20 (3 H, s)) is also formed.

1-Decene: GC column C at 80–170 °C. The formation of 2-decanone was confirmed by ^{1}H NMR and IR of an isolated sample. Control reactions show that 1-decene epoxide and 1-decanal are stable under the reaction conditions. At the end of a catalytic run in toluene, the solvent was evaporated from the homogeneous yellow solution and the resulting oil flash chromatographed to yield the (1-*n*-heptylallyl)chloropalladium dimer $[Pd(CH_2CHCHC_7H_{15})Cl]_2$ (31%) (^{1}H NMR (CCl_4) δ 5.40 (1 H, d of d of d, J = 12, 12, 7 Hz), 4.1–3.5 (1 H, br m), 3.89 (1 H, d, J = 7 Hz), 2.86 (1 H, d, J = 12 Hz), 1.9–1.4 (2 H, br s), 1.6–1.1 (10 H, br s), 0.90 (3 H, br t)).

^{18}O Labeling Study. (a) Infrared. An aliquot of ^{18}O-labeled $Pd(CH_3CN)_2ClNO_2$[1] was converted to the corresponding deuteride by treatment with excess CD_3CN followed by evaporation. (The deuteride was employed in order to avoid interference by the C–H bending modes in the infrared analysis of the ^{18}O content of the nitro group.) Infrared spectra of a CD_3CN solution of the ^{18}O-labeled $Pd(CD_3CN)_2ClNO_2$ so obtained were plotted in absorbance mode and band components resolved and integrated with the aid of a Du Pont curve resolver. Analysis of the high-energy antisymmetric NO_2 stretch (1460 cm^{-1} for $N^{16}O_2$) gave 56% $^{18}O_2$, 3% $^{18}O^{17}O$, 27% $^{18}O^{16}O$, 3% $^{17}O^{16}O$, and 12% $^{16}O_2$. Analysis of the low-energy symmetric NO_2 stretch (1338 cm^{-1} for $N^{16}O_2$) gave 50% $^{18}O_2$, 7% $^{18}O^{17}O$, 27% $^{18}O^{16}O$, 3% $^{17}O^{16}O$, and 13% $^{16}O_2$. The average enrichment calculated from these distributions is 69 ± 2% ^{18}O, 4 ± 1% ^{17}O, and 27 ± 1% ^{16}O.

Reaction of ^{18}O-enriched $Pd(CH_3CN)_2ClNO_2$ (25 mg, 91.6 mmol) and 1-decene (134 mg, 0.955 mmol) in toluene (10 mL) under nitrogen for 48 h, followed by evaporation of solvent and bulb-to-bulb transfer of the residual volatiles gave a mixture of unreacted 1-decene and ^{18}O-labeled 2-decanone. Infrared spectra of a CCl_4 solution of the product plotted in absorbance mode were analyzed as above employing the CO stretching frequency of the 2-decanone. The observed isotope content was 69 ± 1% ^{18}O, 5 ± 1% ^{17}O, and 27 ± 2% ^{16}O.

(b) GC–MS. A similar reaction conducted at 85 °C to maximize epoxide yield was analyzed by GC–MS. Both the 2-decanone and 1,2-epoxydecane were observed to be ^{18}O labeled at approximately the predicted enrichment levels. In particular, the base peak due to the $CH_3O^+{=}CHCH{=}CH_2$ ion was observed at both mass 71 and 73 in the labeled epoxide but only at mass 71 in the unlabeled epoxide.

***tert*-Butylethylene**: GC column C at 30–60 °C. *tert*-Butyl methyl ketone formation confirmed by ^{1}H NMR. At the end of

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a catalytic run in benzene, the solvent was removed from the homogeneous orange solution and the resulting solid flash chromatographed on silica gel to yield a yellow solid containing bis((η^3-2-isopropylallyl)(μ-chloro)palladium(II)) (37%) (^{1}H NMR ($CDCl_3$) δ 3.85 (2 H, s), 2.79 (2 H, s), 2.47 (1 H, sept, J = 6.8 Hz), 1.20 (6 H, d, J = 6.8 Hz)) contaminated with small amounts of other palladium complexes.

Allylbenzene: GC column D at 80–170 °C. Formation of phenylacetone confirmed by ^{1}H NMR.

Styrene: GC column C at 80–170 °C. Formation of acetophenone confirmed by ^{1}H NMR.

Methylenecyclohexane: GC column D at 70–140 °C. Corresponding epoxide formation confirmed by NMR and coinjection on columns A and D.

Cyclopentene: GC column B at 60–140 °C. Cyclopentene epoxide, cyclopentanone, and cyclopentenone formation were confirmed by coinjection on column B. Cyclopent-2-en-1-ol was prepared by several methods but was always contaminated with cyclopentanol and cyclopentenone, and hence the response factor was estimated by comparison with the other C_5 oxygenates and trends observed for the other sized cycloalkene systems.

Cyclohexene: GC column A at 60–140 °C. All products were confirmed by coinjection on column A and cyclohex-2-en-1-ol by ^{1}H NMR.

4-*tert*-Butylcyclohexene: GC column D at 70–160 °C. Epoxide formation was confirmed by coinjection on columns A and D, but the stereochemistry is unknown since the cis and trans epoxides coeluted under all conditions tried.

Cycloheptene: GC column B at 83–149 °C. All oxidation products were confirmed by GC–MS and cycloheptene epoxide by ^{1}H NMR. Authentic cyclohept-2-en-1-ol was prepared from cycloheptene by NBS bromination[48b] followed by alkaline hydrolysis.[49] Cyclohept-2-en-1-one was prepared by Jones CrO_3 oxidation of cyclohept-2-en-1-ol.[48c]

***cis*-Cyclooctene**: GC columns A and D at 90–140 °C. Authentic cyclooct-2-en-1-ol and cyclooct-2-en-1-one were prepared by the same procedures as for the cycloheptene series.

***trans*-Cyclooctene**: GC columns A and D at 90–140 °C. Cyclooctanone formation was confirmed by ^{1}H NMR. In oxidation reactions that employed greater than 1 equiv of *trans*-cyclooctene, rapid isomerization to *cis*-cyclooctene occurred. For this reason, the *trans*-cyclooctene was always dissolved in a small volume of solvent and the mixture added slowly to stirred solutions of 1.

Norbornene: GC columns A and B at 60–150 °C. (Use of Chromosorb P as a support must be avoided to prevent isomerization of epoxynorbornane to norcamphor. *exo*-Epoxynorbornane formation confirmed by ^{1}H and ^{13}C NMR. The composition of isolated norbornene metallacycle 3[3c] (78.8 mg) in toluene (15 mL) under nitrogen at room temperature was monitored by GC. The product epoxide was formed initially at ~ 3%/h, reaching a maximum yield of 90% after 80 h. At longer reaction times some decomposition occurred. The palladium was recovered by filtration in the form of $[Pd(NO)Cl]_n$ (85%).

Bicyclo[2.2.2]octene: GC column B at 60–150 °C. Formation of epoxybicyclo[2.2.2]octane confirmed by ^{1}H NMR.

Bicyclo[3.2.1]octene: GC column B at 60–150 °C. *exo*-Epoxybicyclo[3.2.1]octane formation confirmed by ^{1}H NMR.

(Trimethylsilyl)ethylene. Formation of the highly reactive (trimethylsilyl)acetaldehyde[50] was confirmed by ^{1}H NMR (($CDCl_3$) δ 9.64 (~1 H, t, J = 4.3 Hz), 2.28 (~2 H, d, J = 4.3 Hz), 0.05 (~9 H, s)) and IR ((CH_2Cl_2) 1696 cm^{-1} (ν_{CO})).

$[PdNOCl]_n$ (4). To a suspension of nitro complex 1 (181 mg, 0.672 mmol) in toluene (88 mL) under nitrogen was added 1-decene (1.5 mL, 7.9 mmol). The orange-yellow solution immediately cleared to form a yellow solution, which gradually darkened with formation of a red-brown precipitate. After the mixture was stirred for 1 day, GC analysis indicated at 95% yield of 2-decanone (based on Pd). The reaction mixture was suction filtered in air and the filter cake washed with acetone and dried under vacuum to give $[PdNOCl]_n$ (74 mg, 64%) as a red-brown powder, identified by comparison of its IR spectrum (KBr disk) 1759 (s), 1716 (m, sh), 581 (w), 568 (vw) cm^{-1}) with that of an authentic sample.[6]

An identical reaction run in ethyl acetate for 48 h gave a black precipitate of an unknown nitrosyl complex (55 mg). IR (KBr disk): 1677 (s), 732 (m), 483 (w) cm^{-1}. Anal. Found: Cl, 20.81; N, 4.10; Pd, 63 ($Pd_{2.01}Cl_{1.99}N_{0.99}$). This same species was obtained irratically in reactions run in nonpolar solvents (especially with ethylene) and reproducibly when the literature preparation[6] of $[Pd(NO)Cl]_n$ was allowed to stand overnight under ethylene.

Reoxidation of $[PdNOCl]_n$. A suspension of 4 (68 mg, 0.40 mmol) in toluene (70 mL) was treated with acetonitrile (0.59 mL, 11 mmol) and stirred in air for 5 days. The resulting suspension was suction filtered and the cake washed with acetonitrile until all the yellow color was removed. There remained 2 mg of black solid. The clear, golden yellow filtrate was evaporated to give chloro nitro complex 1 (50 mg, 47%) as fluffy, yellow-orange crystals, identified by comparison of appearance, melting point, and IR spectrum with those of an authentic sample.[3c]

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Registry No. 1, 91547-45-4; $CH_2{=}CH_2$, 74-85-1; $CH_2{=}CHCH_2CH_3$, 106-98-9; $CH_2{=}CH(CH_2)_7CH_3$, 872-05-9; $PhCH_2CH{=}CH_2$, 300-57-2; $PhCH{=}CH_2$, 100-42-5; *cis*-$CH_3CH{=}CHCH_3$, 590-18-1; *trans*-$CH_3CH{=}CHCH_3$, 624-64-6; $CH_2{=}CHCH_3$, 115-07-1; $CH_3C(CH_3)_2CH{=}CH_2$, 558-37-2; $BuOCH{=}CH_2$, 111-34-2; $CH_2{=}C(CH_3)_2$, 115-11-7; methylenecyclohexane, 1192-37-6; cyclopentene, 142-29-0; cyclohexene, 110-83-8; 4-*tert*-butylcyclohexene, 2228-98-0; cycloheptene, 628-92-2; *cis*-cyclooctene, 931-87-3; *trans*-cyclooctene, 931-89-5; cyclohept-2-en-1-ol, 4096-38-2; norbornene, 498-66-8; bicyclo[2.2.2]oct-2-ene, 931-64-6; bicyclo[3.2.1]oct-2-ene, 823-02-9.

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