knowledge, no reaction between HO_2 and Br^- has been observed. This is probably due both to a slow reaction rate and the very rapid oxidation of HO_2 by any of the possible products (Br_2, Br_2^-, and Br_3^-).[25-27] In contrast, the lifetime of superoxotitanium(IV) is long relative to that of HO_2, and the oxidation of the superoxo complex by Br_2 or Br_3^- would be expected to be very slow on the basis of our results with the stronger oxidant Cl_2. We observe a small rate enhancement for both the disappearance of superoxotitanium(IV) and the formation of peroxotitanium(IV) in the presence of 0.1 M bromide ion in molar perchloric acid. Spectral evidence for the concomitant formation of small amounts of Br_2 and Br_3^- was obtained.[28] If we assume that TiO_2^{3+} is the reactive species toward Br^-, as appears to be the case for I^-, then the limited data in Table IV allow an estimate of 2 M^{-1} s^{-1} for the rate constant of the TiO_2^{3+}–Br^- reaction. The rate constant for a possible HO_2–Br^- reaction would not be expected to be very much greater, so it is hardly surprising that this reaction was not observed in the radiolysis experiments.

The multimixing procedure used in this study should be applicable to relatively long-lived superoxo complexes of other d^0 and f^0 metal ions. The technique has been used previously to study reactions of a peroxo–superoxo complex of vanadium(V) formulated as $VO_3^+ \cdot O_2H$.[3] This complex was found to be more susceptible to oxidation than we have observed for superoxotitanium(IV). Measurable rates were obtained with iodine and benzoquinone, although again the rate constants are considerably smaller than for the analogous reactions of HO_2. The technique should also allow studies of the redox properties of unstable peroxo complexes such as $CrO(O_2)_2$.[29] An important objective in these studies is to increase our understanding of how metal ions modify the chemistry of superoxide and peroxide. Both of these dioxygen species are thought to be important intermediates in the water–oxygen cycle.[30-32] The advantage of d^0 and f^0 metal ions is their ability to rapidly form peroxo and superoxo complexes with larger formation constants.[33-35]

Acknowledgment. This research was supported by the U.S. Army Research Office. The kinetic studies with hexachloroiridate(III) were performed by Lisa Schwane and Paul Williams.

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Nickel Catalysis of Olefin Epoxidation

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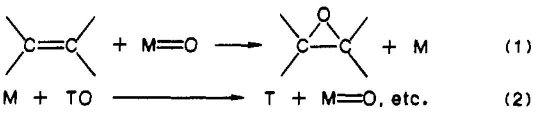
The catalytic epoxidation of olefins is examined with a wide variety of nickel(II) complexes derived from different tetraaza macrocycles (both neutral and anionic), Schiff bases, porphyrins, and bidentate phosphines. The most effective among these are the dicationic $Ni^{II}(cyclam)^{2+}$ and its unsaturated analogues $Ni^{II}(Me_4[14]tetraeneN_4)^{2+}$ and $Ni^{II}(CR)^{2+}$ as well as the Schiff base derivatives Ni^{II}(Tfaced) and Ni^{II}(Aceted). All of the nickel(II) complexes efficiently convert iodosylbenzene as the terminal oxidant to iodobenzene. However, despite extensive efforts to optimize the solvent, counterions, added donor ligands, and terminal oxidants, the conversions of olefins are restricted to modest yields of epoxides owing to competition from the oxidative attack on the solvent and the ligands. The catalytic activity is tentatively ascribed to an active oxo–nickel(IV) intermediate that is rather indiscriminate in oxygen atom transfer and in homolytic attack on solvent as well as ligand. A spectral transient is assigned to a (μ-oxo)nickel(III) dimer arising from the facile association of the putative oxo–nickel(IV) intermediate with the nickel(II) precursor. In these regards, the nickel catalysis of olefin epoxidation is strongly reminiscent of the behavior of cationic manganese(III) complexes under similar conditions.

Introduction

The epoxidation of olefins with terminal oxidants such as peroxides, iodosylbenzene, hypochlorite, amine oxides, etc. is catalyzed by a variety of metal complexes.[1] Metalloporphyrins have been studied extensively owing to their direct relationship to enzymatic oxidations with cytochrome P-450.[2] The same catalytic epoxidations are mimicked by metal complexes of other macrocycles in which (a more or less) square-planar array of nitrogen and oxygen atoms are coordinated to the metal center.[3]

At least three separate pathways have been identified for the catalytic epoxidation of olefins.[1] Among these, the oxygen rebound process outlined in Scheme I is particularly viable.[4,5] According to Scheme I, the metal catalyst (M) serves as a relay for oxygen atom transfer from the oxygen donor (TO) via the intermediacy of an oxo–metal species (M=O). The shuttling of the metal complex between the two states formally corresponds to an oxidative-addition–reductive-elimination sequence. As such, it is generally found that those metals that are capable of readily undergoing two-electron changes, such as iron(III), manganese(III), chromium(III), and ruthenium(IV), are effective in catalysis.[1-7]

Scheme I



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(3) See, e.g.: Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606. Srinivasan, K.; Kochi, J. K. *Inorg. Chem.* **1985**, *24*, 4671.

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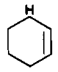
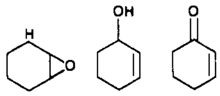
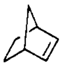
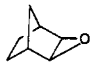
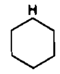
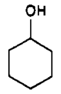
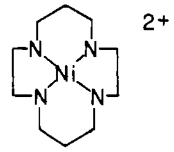
Table I. Comparison of Hydrocarbon Oxidations of $Ni^{II}(cyclam)^{2+}$ with Different Catalytic Systems[a]

		yield, % metal catalyst syst			
hydrocarbon	product	$Ni^{II}(cyclam)^{2+}$, $PhIO$[b]	$Fe^{III}(TPP)^+$, $PhIO$[c]	$Fe^{III}(TPP)^+$, $ArNMe_2O$[d]	$Cr^{III}(TPP)^+$, $PhIO$[e]
		85		90	
	 [f]	69 (36:49:15)	70 (79:21:0)	56 (80:20:0)	66 (4:75:21)
		47[g]		36	99
		10[h]	8	2	0

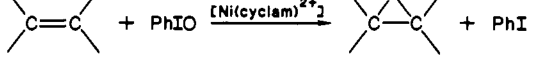
[a] In dichloromethane at ambient temperatures. [b] This work. [c] From ref 17. [d] From ref 18. [e] From ref 19. [f] Relative molar ratios in parentheses. [g] Includes ~5% norbornanone; oxidation carried out with 2 equiv of Et_3PO. [h] Includes 8% cyclohexanone.

In this study we are concerned with the use of nickel(II) complexes for the catalytic epoxidation of olefins for two principal reasons. First, the search for a new epoxidation catalyst is stimulated by the availability of higher oxidation states of nickel(II)—notably as nickel(IV) in hexacoordinate oxime complexes[8] and tetracoordinate diphosphine and diarsine complexes[9] and as Ni(II)–Ni(IV) mixed-valence complexes of ethylenediamine.[10] Heretofore no chemical properties (other than redox)[11] of these nickel(IV) complexes have been reported. Although an oxidant described as nickel peroxide (NiO_2) has been widely used in hydrocarbon oxidations, its composition and structure are uncertain.[12] Second, a variety of nickel(II) complexes with macrocyclic ligands are known to exist with wide variations in redox properties.[9a,13–15] In order to screen the efficacy of these complexes for catalytic activity, we measured the yields of olefin oxides with iodosylbenzene as the terminal oxidant under uniform conditions. Our initial efforts were directed to the nickel(II) complex A of the tetraza macrocycle cyclam[16] (cyclam = 1,4,8,11-tetraazacyclotetradecane).



A

I. Catalytic Activity of Nickel(II) Cyclam. Comparison with Other Epoxidation Catalysts. When a mixture of 0.01 mmol of $Ni^{II}(cyclam)(ClO_4)_2$ (A) and iodosylbenzene (2–3 equiv) was allowed to react with a solution of 1 mmol of tetramethylethylene in dichloromethane (1 mL), a slow reaction ensued to produce the corresponding epoxide in 85% yield according to the stoichiometry in eq 3. Moreover, norbornene oxide was formed in 42% yield when norbornene was treated under similar conditions but with triethylphosphine oxide added as a promoter. Cyclohexene was converted to cyclohexene oxide together with the products of allylic attack, viz., cyclohexen-3-ol and cyclohexen-3-one. The relative distribution among these products was similar to that previously obtained with *meso*-(tetraphenylporphinato)iron(III), $Fe^{III}(TPP)^+$, as the catalyst with either iodosylbenzene or a tertiary amine oxide as the oxygen atom donor.[17,18] Epoxidations carried out with these systems are collected in Table I for the representative olefins as a comparative basis for catalytic efficiency. Indeed, the divergent reactivity patterns that can be obtained during catalytic epoxidations are underscored by the inclusion of the chromium(III) analogue $Cr^{III}(TPP)^+$ in Table I.[19] The varying degrees of attack on a saturated carbon–hydrogen bond are also shown by the oxidative conversion of cyclohexane to cyclohexanol (and cyclohexanone).



$$>C{=}C< + \text{PhIO} \xrightarrow{[\text{Ni(cyclam)}^{2+}]} >C\overset{O}{-}C< + \text{PhI} \qquad (3)$$

Since the orange $Ni^{II}(cyclam)^{2+}$ is readily converted to the green paramagnetic $Ni^{III}(cyclam)^{3+}$, we independently prepared the trication as the perchlorate salt[20] for a test of its catalytic activity. When an intense green solution of 0.01 M $Ni^{III}(cyclam)^{3+}$ in acetonitrile was treated with a 10^2-fold excess of norbornene and excess iodosylbenzene, only small amounts of norbornene oxide (~1%) were formed. Slightly better yields of epoxide (~7%) were obtained in dichloromethane but did not rival those obtained with the nickel(II) salt. Accordingly, all further catalytic studies were carried out with nickel(II) complexes.

At this juncture it is necessary to distinguish the *catalytic activity* of a nickel complex based on the conversion of the terminal oxidant from its *catalytic efficiency* for oxygen atom transfer to olefins. With iodosylbenzene, the activity was evaluated by the amount of iodobenzene formed, and the efficiency was determined by molar yield of epoxide relative to iodobenzene (see eq 3), as measured by direct GC–MS analysis of the reaction mixture. (Note that the insolubility of iodosylbenzene[3] allows its easy removal prior to analysis.)

II. Structural Variations in Nickel(II) Catalysts. The comparative results in Table I indicated that the effectiveness of

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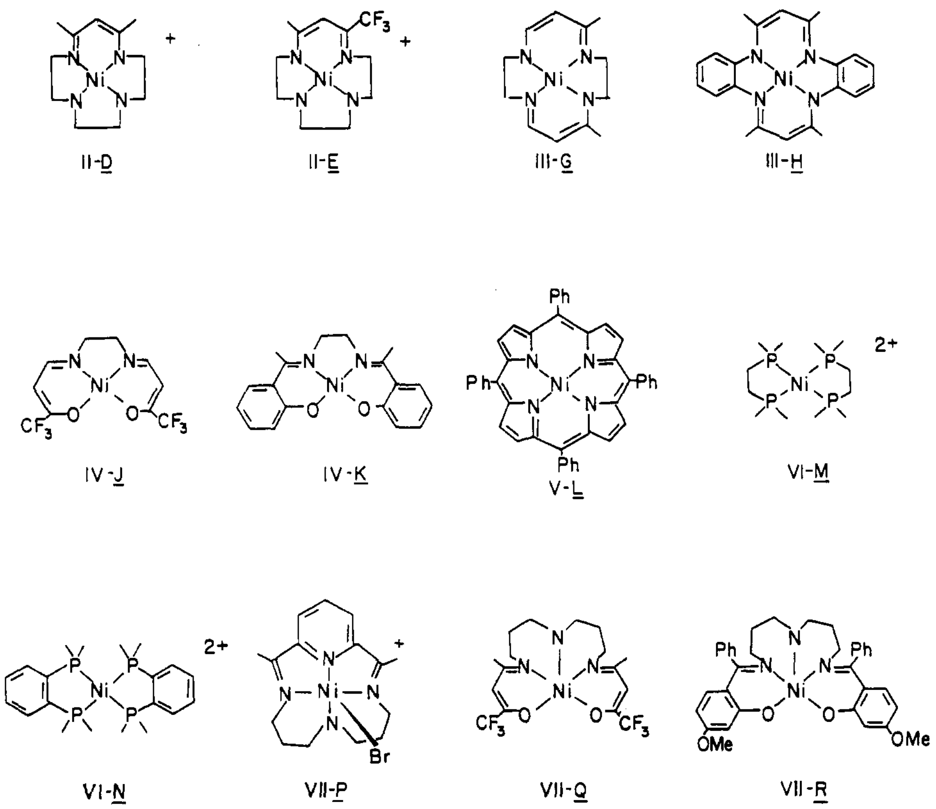
Chart I. Nickel(II) Complexes for Catalysis of Olefin Epoxidation[a]



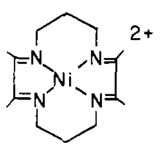
II-D II-E III-G III-H

IV-J IV-K V-L VI-M

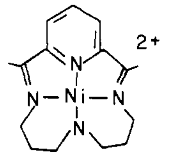
VI-N VII-P VII-Q VII-R

[a] For reference to the acronyms, see the nomenclature in the Experimental Section.

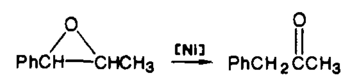
$Ni^{II}(cyclam)^{2+}$ for catalytic epoxidation was not strongly differentiated from that of the more conventional systems based on $Fe^{III}(TPP)^+$ and $Cr^{III}(TPP)^+$. Accordingly, we examined the catalytic efficiencies of a pair of analogous dicationic nickel(II) complexes B and C of the unsaturated tetraza macrocycles $Me_4[14]tetraeneN_4$[21] and CR[22] ($Me_4[14]tetraeneN_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; CR = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene). The results shown in Table II indicate that the nickel(II) complexes B and C are comparable to $Ni^{II}(cyclam)^{2+}$ with some minor variations. Under these conditions the epoxidation of (*E*)-β-methylstyrene led to the trans epoxide with contamination by <1% *cis*-β-methylstyrene oxide. On the other hand, (*Z*)-β-methylstyrene afforded a ~2:1 mixture of the cis and trans epoxides. Since the driving forces for cis → trans conversions are greater than the converse, we interpret these results as epoxidations that are selective but not highly stereospecific. Furthermore, the isomerization of the epoxide under the catalytic conditions was indicated by the observation of increasing amounts of phenylacetone as the epoxidation of β-methylstyrene progressed. Some of this side product is undoubtedly derived from the Lewis-acid-catalyzed rearrangement of the epoxide, i.e.



B



C

 (4)

$$PhCH(O)CHCH_3 \xrightarrow{[Ni]} PhCH_2C(=O)CH_3 \quad (4)$$

since it is reduced markedly by the addition of additives such as triethylphosphine oxide and pyridine *N*-oxide (See Experimental Section). In the latter case, oxidative cleavage of the C=C bond to benzaldehyde was observed. The detection of pyridine suggests a process similar to that previously observed during chromium(III) catalysis,[3] i.e.

$$PhCH{=}CHCH_3 + PhIO + pyO \xrightarrow{[Ni]} PhCH{=}O + PhI + py + CH_3CHO \quad (5)$$

In each case, the production of large amounts of iodobenzene indicated that the nickel catalysts in Table II were all effective in the reduction (>90%) of the terminal oxidant.

In order to evaluate the effect of other ligand structures on the catalytic efficiency of nickel(II) complexes, we synthesized various types of closed and open macrocyclic derivatives. These nickel(II) complexes were differentiated by classifying them into seven arbitrary categories. Class I consisted of the square-planar dications A, B, and C, as described above. Class II consisted of the monocations D and E[23] (see Chart I). The uncharged nickel(II) tetraza macrocycles G[24] and H[25] as well as the Schiff base analogues J[26] and K[27] were included in classes III and IV, respectively. Class V was represented by the *meso*-tetraphenylporphyrin derivative L.[28] The phosphine complexes M[29] and N[9a] (class VI) were related to those in which nickel(IV) species have been reported.[9] Finally, the last category included the pentacoordinate complexes P,[22] Q,[30] and R.[31] To facilitate

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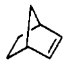
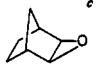
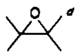
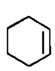
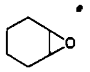
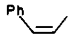
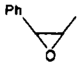
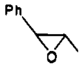
Table II. Catalytic Epoxidations with the Macrocyclic Derivatives of Nickel(II) Dications[a]

olefin	product	catalytic efficiency, %[b] Ni(II) catalyst A	B	C
	 [c]	29	20	25
	 [d]	85		
	 [e]	47 (68:28:4)	20 (60:35:5)	33 (61:33:6)
		38[f] (28)[g]		24
		36[h] (45)[i]		

[a] In dichloromethane (5 mL) containing 0.01 mmol of the Ni(II) complex, 0.15 mmol of iodosylbenzene, and 1.0 mmol of olefin at 25 °C for 2–5 h, unless stated otherwise. [b] As combined products of oxidation, as listed. [c] Includes 2–5% norbornanone. [d] A yield of 19% epoxide formed in the absence of catalyst. [e] In acetonitrile; includes epoxide, cyclohexen-3-ol, and cyclohexen-3-one, with relative ratios in parentheses. [f] After 12 h; e.g., 9% cis epoxide, 5% trans epoxide, and 0% phenylacetone after 2 h, but 7%, 0%, and 26% after 9 h. [g] In the presence of 10 equiv of Et_3PO: 13% cis epoxide, 5% trans epoxide, 7% phenylacetone, and 3% benzaldehyde. [h] After 48 h. Only trans epoxide formed initially, which rearranged completely to phenylacetone with the progress of reaction. [i] In the presence of 2 equiv of pyO: 29% trans epoxide, <0.1% cis epoxide, and 16% benzaldehyde.

comparison, we examined the catalytic efficiency of these nickel(II) complexes, in the epoxidation of norbornene under a standard set of reaction conditions. Although the results in Table III showed a rather wide variation in the yields of norbornene oxide with the various nickel(II) complexes, none could be considered to be an effective catalyst. Moreover, there was no correlation of the catalytic efficiency of the nickel(II) complex with the ease of oxidation as measured by the electrode potential for the Ni(II)/Ni(III) interconversion (see columns 3 and 7). Note that the potentials for the Ni(III)/Ni(IV) interconversion were not available except for the complex N in class VI. It is important to emphasize that all of the nickel(II) complexes in Table III effectively converted iodosylbenzene to high yields (>90%) of iodobenzene.

III. Effect of Reaction Conditions on the Catalytic Epoxidation of Norbornene with Ni^{II}(cyclam)$^{2+}$. Owing to the rather modest yields of epoxides obtained with the various nickel(II) complexes listed in Tables II and III, we sought various changes in reaction conditions to achieve higher catalytic efficiency. Accordingly, we selected Ni^{II}(cyclam)$^{2+}$ as one of the more effective catalysts in Table III to optimize the epoxidation of norbornene. These include the variations of (a) the solvent, (b) the counteranion, (c) the donor ligand, (d) the terminal oxidant, and (e) the temperature, as discussed individually below.

(a) Solvent Effect. The orange perchlorate salt of Ni^{II}(cyclam)$^{2+}$ is soluble in acetonitrile. When a 0.01 M solution of the nickel(II) complex in acetonitrile containing 1 M norbornene was stirred with various amounts of iodosylbenzene, the initially pale green solution (of the bis(acetonitrile) complex) turned light orange accompanied by the dissolution of iodosylbenzene. When 1 equiv of iodosylbenzene was initially added, complete dissolution required 20 min, but the second 1 equiv of added iodosylbenzene dissolved within 10 min. Each incremental addition of iodosylbenzene was followed by the gas chromatographic analysis of both norbornene oxide and iodobenzene. The results in Table IV indicate that essentially no norbornene oxide was formed upon the addition of the first 1 equiv of iodosylbenzene. Thereafter, a relatively constant yield of 12–15% of epoxide was generated with each molar increment of iodosylbenzene. Although the epoxide yields were low, the catalytic activity of Ni^{II}(cyclam)$^{2+}$ in a homogeneous system was unmistakable. By contrast, the reactions carried out in dichloromethane under the conditions described in Table II were partially heterogeneous owing to the limited solubility of the perchlorate salt. The yields of norbornene oxide in both *N,N*-dimethylformamide (DMF) and methanol were nil despite the solubility of Ni^{II}(cyclam)$(ClO_4)_2$ in these media (see Table V).

(b) Anion Effect. In order to determine whether the increased yields of epoxide in dichloromethane and ethylene dichloride were due to partial solubility, we synthesized other salts of Ni^{II}(cyclam)$^{2+}$. Among these, the trifluoromethanesulfonate (triflate, OTf) salt Ni^{II}(cyclam)$(OTf)_2$ was sufficiently soluble in di-

Table III. Epoxidation of Norbornene with the Aid of Various Nickel(II) Complexes[a]

Ni(II) class	catalyst complex	Ni^{II}/Ni^{III} [b]	NBO yield[c]	Ni(II) class	catalyst complex	Ni^{II}/Ni^{III} [b]	NBO yield[c]
I	A	0.67	24	IV	J	1.42	35
	B	1.00	18		K		17
	C	1.03	21				
				V	L	0.56	0
II	D	0.27	0				
	E		6	VI	M		0
					N	0.36[d]	<5
III	G	-0.33	0				
	H	0.60	5	VII	P		0
					Q		0
					R		3

[a] In dichloromethane (1 mL) containing 0.01 mmol of the Ni(II) complex, 0.03 mmol of iodosylbenzene, and 1.0 mmol of norbornene for 2–4 h at 25 °C. [b] $E_{1/2}$ value for Ni(II) → Ni(III) conversion in V vs. Ag/Ag^+ taken from ref 9a, 13–15. [c] Percent molar yield of norbornene oxide (NBO) based on iodobenzene formed. [d] Potential vs. standard calomel electrode; potential for Ni^{III}/Ni^{IV} is 1.18 V vs. SCE.

Table IV. Epoxidation of Norbornene with Ni^{II}(cyclam)$^{2+}$ in Acetonitrile Solution by Incremental Additions of Iodosylbenzene[a]

	amt of iodosylbenzene, 10^2 mmol		amt of iodobenzene, 10^2 mmol		amt of norbornene oxide, 10^3 mmol	
expt	total	increment	total	increment	total	increment (%)[b]
I	1.44	...	0.84	...	0	...
	2.36	1.22	1.97	1.13	1.2	1.2 (12)
	3.76	1.40	3.35	1.38	2.6	1.4 (10)
	5.09	1.33	5.06	1.71	4.9	2.3 (13)
	7.36	2.27	7.73	2.67	9.0	4.1 (15)
II	14.0	...	12.42		17.3	(14)

[a] In acetonitrile (1 mL) containing 1×10^{-2} mmol of Ni^{II}(cyclam)$(ClO_4)_2$ and 1 mmol of norbornene at 25 °C. [b] Based on iodobenzene formed.

Table V. Solvent and Solubility Effects in Norbornene Epoxidation with Various $Ni^{II}(cyclam)X_2$ Salts[a]

X	NBO yield, %[c] solvent[b] CH_2Cl_2	$(ClCH_2)_2$	MeCN	DMF	MeOH
ClO_4^-	24 (p)	22 (p)	8 (s)	<2 (s)	<1 (s)
$CF_3SO_3^-$	18 (s)	17 (s)	7 (s)	<0.5 (s)	<0.5 (s)
BPh_4^-	<1 (n)	<1 (n)	<2 (n)	<0.5 (n)	<0.5 (n)
PF_6^-	19 (p)	19 (p)	10 (p)	<0.5 (s)	<0.5 (s)
Cl^{-}[d]	10 (p)	9 (p)	18 (p)	<2 (s)	<0.5 (s)

[a] In 1.0 mL solvent with 1×10^{-2} mmol of the nickel(II) salt and $(3-5) \times 10^{-2}$ mmol of PhIO at 25 °C. [b] Solubility (qualitative colorimetric) in parentheses: s, soluble; p, partially soluble, n, insoluble. [c] Norbornene oxide (NBO) yield based on iodobenzene formed. [d] As the coordination complex.

Table VI. Effects of Added Donors and Terminal Oxidants on Norbornene Epoxidation with $Ni^{II}(cyclam)$[a]

terminal oxidant	added donor	amt of donor, equiv[b]	NBO yield, %[c] CH_2Cl_2	MeCN
C_6H_5IO	none		24	14
	Et_3PO	1	36	22
		2	42	22
		4	18	...
		8	16	...
	DMF	1	36	6
		5	29	6
		25	14	6
	pyO	1	...	22
		4	...	16
	py	1	...	0
	imidazole	1	...	0
C_6F_5IO	none		24[d]	0
$C_6H_5I(OAc)_2$	none		7	4
p-$NCC_6H_4NMe_2O$	none		0	...

[a] In 1.0 mL of solvent containing 1×10^{-2} mmol of $Ni^{II}(cyclam)(ClO_4)_2$ and 3×10^{-2} mmol of terminal oxidant at 25 °C. [b] Relative to added nickel(II) salt. [c] Based on iodobenzene formed, unless indicated otherwise. [d] Based on pentafluoroiodobenzene formed. The yield of NBO was <0.2% in the presence of $MeOH/H_2O$.[32]

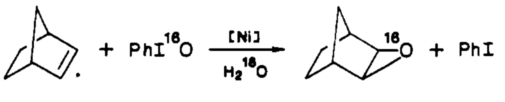
chloromethane and ethylene dichloride to carry out the catalysis under homogeneous conditions. In fact, the results in Table V show that somewhat lower yields of epoxide were generated in these homogeneous systems. The solubility effects of the other salts of $Ni^{II}(cyclam)^{2+}$ in several solvents are also summarized in the table.

(c) Effects of Added Donor Ligands. The addition of 1 equiv of triethylphosphine oxide to $Ni^{II}(cyclam)(ClO_4)_2$ in dichloromethane led to the enhancement of the epoxide yield from 24 to 36%. The yield was increased further to 42% in the presence of 2 equiv of Et_3PO. However, additional Et_3PO caused the yield of norbornene oxide to decrease as shown in Table VI. The addition of small amounts of DMF as a donor ligand had similar effects. The promotion by added donors was similar but less pronounced for epoxidations carried out in acetonitrile. The relatively strong bases pyridine and imidazole inhibited the formation of epoxide.

(d) Terminal Oxidants. Variation of the oxygen atom donor did not materially enhance the epoxide yield. The results in Table VI show that the perfluorinated analogue[32] was indistinguishable from iodosylbenzene in dichloromethane and ineffective in acetonitrile. Furthermore, the tertiary amine oxide *p*-$NCC_6H_4NMe_2O$[33] was without effect.

When the catalytic epoxidations were carried out at 0 °C in an ice bath, prolonged stirring was required to achieve the requisite amounts of iodobenzene. Otherwise no significant changes in the epoxide yields were noted.

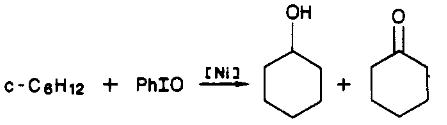
IV. Incorporation of Isotopic Oxygen-18 from Labeled Water. The course of oxygen atom transfer during catalysis was examined by the incorporation into the epoxide of the isotopic oxygen-18 from labeled water. In a typical experiment, 0.01 mmol of $Ni^{II}(cyclam)(ClO_4)_2$ and 1.0 mmol of norbornene was dissolved in acetonitrile (1 mL) containing 1.85 mmol of labeled water (90% enrichment). After reaction with 0.02 mmol of iodosylbenzene, the reaction mixture was subjected to GC-MS analysis for norbornene oxide-^{16}O and -^{18}O by the relative abundances of the principal mass ion peaks at *m*/*z* = 110 and 112, respectively. The isotopic composition of ~80% for the labeled norbornene oxide indicated that a major fraction of the oxygen was derived from water, i.e.



(6)

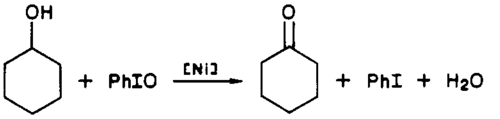
Control experiments established that neither prior exchange of the iodosylbenzene nor subsequent exchange of the epoxide with the labeled water had occurred under the reaction conditions.

V. Alkane Oxidation during $Ni^{II}(cyclam)^{2+}$ Catalysis. The oxidation of saturated carbon-hydrogen bonds, as in the allylic attack of cyclohexene in Table V, was further examined with cyclohexane as the substrate. Thus, the exposure of a solution of cyclohexane (0.3 mmol) in dichloromethane (5 mL) to a slurry of iodosylbenzene (0.15 mmol) and $Ni^{II}(cyclam)(ClO_4)_2$ (0.01 mmol) led to a mixture of cyclohexanol and cyclohexanone in 2 and 8% yields, respectively:



(7)

When the same combination was carried out under homogeneous conditions in acetonitrile solution, only cyclohexanone was observed in 2% yield. Separate experiments indicated that cyclohexanol was oxidatively converted to cyclohexanone under the catalytic conditions, i.e.



(8)

Since the yields of cyclohexanol and cyclohexanone were based on the amount of iodobenzene formed, most of the terminal oxidant was converted by other pathways, some of which are described below.

VI. Reduction of Iodosylbenzene with Nickel(II) Cyclam in the Absence of Hydrocarbon Substrates. The epoxidations of olefins as they are induced by iodosylbenzene and nickel(II) were limited to the modest yields of the products reported in Tables II and III. Nonetheless, the catalytic *activities* of these systems are rather high, as attested by the uniformly excellent conversions of the terminal oxidant to the reduced iodobenzene. In order to probe the limitations of nickel(II) complexes as epoxidation catalysts, we carefully examined the reaction of $Ni^{II}(cyclam)^{2+}$ directly with iodosylbenzene in the absence of hydrocarbons. Thus when a pale green solution of 0.01 M $Ni^{II}(cyclam)(ClO_4)_2$ in acetonitrile was treated with 1 equiv of iodosylbenzene, the dissolution was accompanied by the development of an orange color (showing weak bands at ~285 and 385 nm in the electronic spectrum). The intensity of the color increased when more iodosylbenzene was added, and by the time more than 7 equiv of PhIO had been added, the rate of dissolution was extremely slow and there was a nominal discharge of color. The orange solution was EPR-silent. Furthermore, the absorption bands at ~285 and 385 nm were unaffected by the addition of either norbornene or phenyldimethylphosphine, and no epoxide or phosphine oxide was observed as products. Workup of the orange solution by removal in vacuo

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(32) (a) Traylor, P. S.; Dolphin, D.; Traylor, T. G. *J. Chem. Soc., Chem. Commun.* **1984**, 279. (b) Traylor, T. G.; Marsters, J. C., Jr.; Nakano, T.; Dunlap, B. E. *J. Am. Chem. Soc.* **1985**, *107*, 5537.

(33) Dicken, C. M.; Lu, F.-L.; Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 5776.

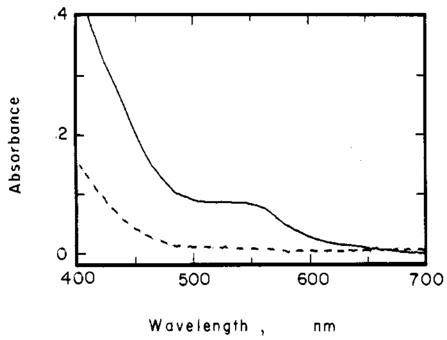


Figure 1. Transient absorption spectrum (—) obtained from equimolar solution of 5×10^{-3} M $Ni^{II}(cyclam)(OTf)_2$ and *m*-chloroperbenzoic acid in dichloromethane at −78 °C and spectrum (- - -) obtained after the addition of 5 equiv of phenyldimethylphosphine.

of the solvent and other volatiles (including iodobenzene) afforded a brown solid. The IR spectum was similar to that of $Ni^{II}(cyclam)(ClO_4)_2$ but in addition showed an intense band at 1647 cm^{-1}. The latter is indicative of the introduction of unsaturation into the ligand, most likely as a C=N bond, similar to that (at 1656 cm^{-1}) introduced during nitric acid oxidation of II-C.[34] Unfortunately, the isolation of the free ligand by treatment of the solid with sodium cyanide, a procedure that has been successfully utilized for $Ni^{II}(cyclam)^{2+}$,[16b,35] led to only a small amount of an uncharacterized oil.

In an attempt to observe the initial reactive intermediate in nickel catalysis, we replaced iodosylbenzene with *m*-chloroperbenzoic acid (MCPBA), which is a more active oxygen atom donor. Indeed, a transient intermediate (pink) was observed immediately when $Ni^{II}(cyclam)^{2+}$ was treated with an equimolar amount of MCPBA in acetonitrile. However, the intermediate was too unstable even at −40 °C for epoxidation studies to be carried out. Thus, a suspension of $Ni^{II}(cyclam)(ClO_4)_2$ in dichloromethane was treated with an equimolar amount of MCPBA at −78 °C. The initial yellow slurry changed to pink-violet, but this mixture did not react with cyclohexene. Similarly, the treatment of a pale yellow solution of $Ni^{II}(cyclam)(OTf)_2$ in dichloromethane with MCPBA at −78 °C afforded a light pink solution showing a weak absorption band at ~550 nm, as shown in Figure 1. The band disappeared completely upon the addition of phenyldimethylphosphine, and we judge from the resultant yellow solution that $Ni^{II}(cyclam)^{2+}$ was regenerated. GC–MS analysis of the reaction mixture qualitatively indicated the formation of triethylphosphine oxide in high yields (>80%). The absorption band at 550 nm was unaffected by the addition of excess cyclohexene, and no epoxide was detected.

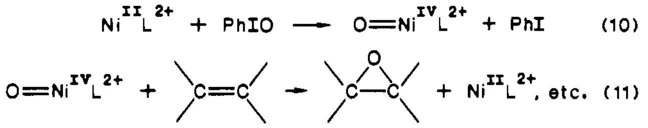
Discussion

The search among the large number of nickel(II) complexes A–R with different types of ligands has failed to produce a catalyst that converts olefins to high yields of epoxides with iodosylbenzene as the terminal oxidant. Nonetheless, our extensive efforts to optimize the catalytic efficiency have provided some valuable insight into the viability of this oxidative system, which merits further discussion. Foremost among these is the conclusion that the nickel(II) macrocycles are involved in oxygen atom transfer to olefins. The limited yields of epoxides are not due to an inactive catalyst. Quite the contrary, they suffer from a *too active* system. Thus we find that essentially all the nickel(II) complexes are capable of readily utilizing the terminal oxidant. This is always apparent in the rapid rate of reductive dissolution of iodosylbenzene (which has limited solubility in both acetonitrile and dichloromethane) to iodobenzene in the presence of the nickel(II) complexes. Since the epoxide yields are based on the amount of iodobenzene formed, the sizable deficit in the oxidation equivalents is attributable to effective competition from solvent or ligand oxidation (and other pathways[36]). The results in Table IV support both oxidative side reactions. Thus the first 1 equiv of iodosylbenzene is responsible for ligand oxidation without producing epoxide. The subsequent increments are uniformly diverted by solvent attack (~80–85%). Isolation and spectral studies carried out in the absence of olefinic substrate (vide supra) indicate that ligand oxidation probably involves a dehydrogenation of the cyclam to incorporate an unsaturation linkage, as previously described in related examples.[34] The oxidative attack on the solvent has been difficult to establish with certainty.[3,7] However, the conversion of cyclohexane to a mixture of cyclohexanol and cyclohexanone suggests that unactivated carbon–hydrogen bonds are susceptible to this catalytic system.[37] Thus, the identification of hydrogen cyanide from acetonitrile and carbon dioxide from dichloromethane supports a similar process occurring in these solvents,[38] e.g.

$$CH_3CN + PhIO \xrightarrow{[Ni]} PhI + HOCH_2CN \xrightarrow{fast} HCN + CH_2O \quad (9)$$

Be that as it may, we inquire as to what is the nature of the reactive nickel intermediate that leads to epoxidation and to solvent and ligand attack. Since the rapidity of the catalytic steps precluded the direct observation of intermediates, we must rely on indirect evidence for the active nickel species. Accordingly, we proceed from the observation that the accumulated results of the reactivity patterns and the effects of donor ligands in this study are strongly reminiscent of the behavior of manganese(III) catalysts previously observed under similar conditions.[7] As such, (μ-oxo)nickel species as well as their iodosylbenzene adducts are related to the manganese analogues, which have been isolated.[39] In both cases the most direct reaction pathway involves a reactive intermediate such as an oxo–nickel species in the oxygen rebound process outlined in Scheme I. As applied to the nickel(II) cyclam dication, oxygen atom transfer from iodosylbenzene would proceed as shown in Scheme II, where L represents cyclam or dehydrocyclam (vide supra). The oxo–nickel intermediate is formed from iodosylbenzene by a process (eq 10) which is analogous to that previously established for the related cationic chromium(III) complexes.[3] The driving force for such a transformation is no doubt derived from electron accession from the ligand to the metal center. Although there is no general correlation with the Ni^{II}/Ni^{III} potential, it is interesting to note that the active nickel(II) complexes of class I are characterized by the relatively high ligand field strengths of the macrocycles, as evaluated by the parameter $Dq^{xy} > 1400\ cm^{-1}$.[40]

Scheme II



The pathway outlined in Scheme II provides a ready explanation for five important facets of nickel catalysis through the agency of a single intermediate.

(i) An oxo–nickel dication would be capable of isotopic exchange with ^{18}O-enriched water, i.e.

$$O{=}Ni^{IV}L^{2+} + H_2{}^{18}O \rightleftharpoons {}^{18}O{=}Ni^{IV}L^{2+} + H_2O \quad (12)$$

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(34) (a) Barefield, E. K.; Lovecchio, F. V.; Tokel, N. E.; Ochiai, E.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 283. (b) See also ref 20a.

(35) Wagner, F.; Barefield, E. K. *Inorg. Chem.* **1976**, *15*, 408.

(36) (a) Chevrier, B.; Weiss, R. *J. Am. Chem. Soc.* **1976**, *98*, 2985. (b) Balch, A. L.; Chan, Y.-W.; Olmstead, M. M. *J. Am. Chem. Soc.* **1985**, *107*, 6510. (c) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3771. (d) The absence of dioxygen precludes a metal-catalyzed disproportionation of iodosylbenzene; i.e., $2PhIO \xrightarrow{[Ni]} O_2 + 2PhI$. Furthermore, a catalytic disproportionation to iodoxybenzene (insoluble) is unlikely in view of the excellent yields (>95%) of iodobenzene obtained.

(37) Cf.: (a) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515. (b) Suslik, K.; Cook, B.; Fox, M. *J. Chem. Soc., Chem. Commun.* **1985**, 580.

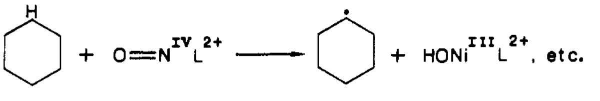
(38) Michaud, P.; Srinivasan, K., unpublished results.

(39) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3510.

(40) Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2968.

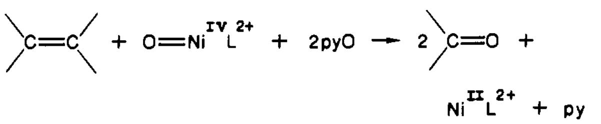
in comparison with the behavior of the analogous oxo–chromium(V) cation noted earlier.[3] The facile exchange in eq 12 could account for the efficient ^{18}O incorporation of labeled water into the epoxide in the catalytic process (vide supra). Such an isotopic incorporation in eq 12 is consistent with an independent oxo–nickel intermediate. An alternative pathway via a prior exchange[2b] with the terminal oxidant is ruled out.

(ii) Oxygen atom transfer from the oxo–nickel intermediate (eq 11) may occur in competition with attack on ligand and solvent. The latter can be considered in the context of hydrogen atom abstraction, as exemplified in the oxidative conversion of cyclohexene to cyclohexenol and cyclohexane to cyclohexanol (and further oxidation to their ketones). Such oxidative transformations have also been observed during manganese catalysis.[7,37,41] As applied to this study, the homolytic process commences with eq 13. We judge from the extensive diversion of the terminal oxidant



(13)

to such side reactions that the oxo–nickel(IV) species is somewhat more prone to this type of homolytic process than it is to oxygen atom transfer to the olefinic substrate. Furthermore, the oxidative cleavage of the C═C bond in *β*-methylstyrene when the catalysis is carried out with pyridine *N*-oxide (see eq 5) compares with the process established for the related oxo–chromium(V) species,[3] i.e.



(14)

(iii) Various attempts were made to spectrally observe the reactive intermediate responsible for epoxidation. Thus, the fleeting pink species generated in Figure 1 from $Ni^{II}(cyclam)^{2+}$ and *m*-chloroperbenzoic acid at −78 °C had an absorption spectrum ($\lambda_{max} \cong 550$ nm) expected for a product of oxidative addition to nickel(II).[42] However, its inability to epoxidize norbornene precludes it as the viable intermediate. Nonetheless, the formation of phosphine oxide from phenyldimethylphosphine is consistent with this species containing an active oxygen. Again this behavior is akin to that observed during manganese catalysis and is attributed to the (μ-oxo)manganese dimer. As applied to this study, the relevant transient is the (μ-oxo)nickel(III) dimer formed by a process analogous to that presented earlier,[7] viz.

$$O{=}Ni^{IV}L^{2+} + Ni^{II}L^{2+} \rightarrow LNi^{III}ONi^{III}Li^{4+} \qquad (15)$$

According to this formulation, the active oxo–nickel(IV) would be observed only as a more persistent (μ-oxo)nickel(III) dimer, especially in the absence of reactive substrates. By comparison with the analogous manganese species, it could be capable of oxygen atom transfer to an active acceptor such as a phosphine, e.g.

$$LNi^{III}ONi^{III}L^{4+} + PMe_2Ph \rightarrow OPMe_2Ph + 2Ni^{II}L_2{}^{2+} \qquad (16)$$

The absorption spectra of oxo–nickel(IV) and oxo–nickel(III) species are likely not to be very different.[42]

(iv) The comparative studies of the perchlorate and triflate salts of $Ni^{II}(cyclam)^{2+}$ in dichloromethane indicate that the best yields of epoxide are obtained by and large under conditions in which the nickel(II) salt is only partially soluble (see Table V). Such an observation can be accommodated by an active intermediate such as an oxo–nickel species that is diverted by the nickel(II) reactant. Indeed, the formation of the (μ-oxo)nickel dimer in eq 15 would be promoted by the relatively high concentrations of $Ni^{II}(cyclam)^{2+}$ made possible by the soluble triflate salt. As such, optimum conditions for oxygen atom transfer from the active oxo–nickel species call for low steady-state concentrations of nickel(II) as in the partially soluble perchlorate salt.

(v) The stereochemistry of epoxide formation in Table II indicates predominant, but not exclusive, retention of configuration at the trigonal carbon centers. This, together with the observation of skeletal rearrangement of the olefin moiety as in eq 4, is akin to the behavior of the oxo–chromium(V) intermediate in the catalytic epoxidation of olefins with iodosylbenzene.[3] As applied to the catalytic system studied here, the stereochemistry and skeletal rearrangement would be derived from the prior addition of the oxo–nickel intermediate to the olefinic substrate. The resulting adduct is capble of isomerization by α,β bond rotation and skeletal rearrangement from a carbocationic center, as elborated earlier.[3]

The postulation of oxo–nickel(IV) species thus allows all of the diverse experimental facets of nickel catalysis to be consistently accommodated within a single mechanistic framework. However, we hasten to add that there are other possibilities, the foremost of which includes the oxygen atom transfer from a labile nickel(II) complex of iodosylbenzene. The latter is related to stable adducts previously isolated from manganese(III) porphyrin[39] and to transient adducts recently detected from binuclear copper(II) complexes.[43] The mechanistic pathway by which such iodosylbenzene complexes can transfer an oxygen atom directly to an olefin, without the agency of an oxo–metal intermediate, is less clear.[44] Further studies are required to elucidate such mechanistic details.

Conclusions

The catalytic properties of nickel(II) are qualitatively changed by complexation to tetraaza macrocycles and the other ligands listed in Table III. Thus, Valentine and co-workers[45] previously showed that soluble nickel(II) salts (unlike their iron(II), manganese(II), cobalt(II), and copper(II) counterparts) are completely ineffective in the catalytic epoxidations of olefins with iodosylbenzene. By contrast, we find that the nickel(II) macrocycles, particularly the dications in class I and the salen derivatives in class IV, are active catalysts for the decomposition of terminal oxidants such as iodosylbenzene. Their ability to effect the catalytic epoxidation of olefins is limited by the high reactivity of a putative oxo–nickel(IV) intermediate owing to facile side reaction, which we ascribe to (a) homolytic reactions with ligands and solvents as in eq 13 and (b) the ready formation of (μ-oxo)nickel dimers as in eq 15. We believe that the synthesis of other cationic nickel(II) complexes, such as those with "picket-fence" ligands,[46] could provide the means to develop more useful catalysts for epoxidation.

Experimental Section

Materials. Iodosylbenzene was prepared from iodosylbenzene diacetate (Aldrich).[47] Pentafluoroiodosylbenzene was prepared from pentafluoroiodobenzene (Aldrich) via the bis(trifluoroacetate) by nitric acid oxidation.[48] *p*-Cyano-*N*,*N*-dimethylaniline *N*-oxide was obtained from the oxidation of the amine (Aldrich) with *m*-chloroperbenzoic acid (MCPBA; Aldrich, 80–85%).[33] Labeled water ($H_2{}^{18}O$) of 90% isotopic purity was obtained from Aldrich and used as such. The hydrocarbon substrates obtained from the previous studies[3,7] were distilled from lithium aluminum hydride and stored in Schlenk flasks under argon. Triethylphosphine oxide and pyridine-*N*-oxide (pyO) were obtained from a previous study.[3]

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(42) Compare: Carnieri, N.; Harriman, A.; Porter, G. *J. Chem. Soc., Dalton Trans.* **1982**, 931. Carnieri, N.; Harriman, A.; Porter, G.; Kalyanasundaram, K. *J. Chem. Soc., Dalton Trans.* **1982**, 1231.

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The nickel(II) complexes were obtained as follows. **Ni(cyclam)(ClO$_4$)$_2$ (I-A)**, or (1,4,8,11-tetraazacyclotetradecane)nickel(II) perchlorate, was prepared from 1,5,8,12-tetraazadecane by condensation with glyoxal in the presence of Ni(ClO$_4$)$_2$ followed by borohydride reduction.[16b] It was converted to the trifluoromethanesulfonate (triflate) salt by ion exchange over Dowex 50 and dried over P$_2$O$_5$. The orange-yellow Ni(cyclam)(PF$_6$)$_2$ and the pale yellow Ni(cyclam)(BPh$_4$)$_2$ were obtained by metathesis of the perchlorate in aqueous solution with NH$_4$PF$_6$ and NaBPh$_4$, respectively. The mauve Ni(cyclam)Cl$_2$ was also prepared from the perchlorate in methanol by the addition of lithium chloride.[16a] **Ni(Me$_4$[14]tetraeneN$_4$)ZnCl$_4$ (I-B)**, or (2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)nickel(II) tetrachlorozincate, was obtained as dark brown crystals from the condensation of 2,3-butanedione with 1,3-diaminopropane in the presence of Ni(OAc)$_2$·4H$_2$O.[21] **Ni(CR)(ClO$_4$)$_2$ (I-C)**, or {2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene}nickel(II) perchlorate, was prepared as brick red microcrystals from 2,6-diacetylpyridine and 3,3′-iminobis(propylamine) and NiCl$_2$·6H$_2$O followed by the addition of NaClO$_4$.[22] It was converted to the bromo derivative **[Ni(CR)Br]ClO$_4$ (VII-P)** by addition of NaBr to an aqueous solution.[22] **Ni(AT)ClO$_4$ (II-D)**, or [11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienato(1−)]nickel(II) perchlorate, was prepared from triethylenetetramine and Ni(OAc)$_2$·4H$_2$O with 2,4-pentanedione followed by NaClO$_4$.[23] **Ni(TAT)BF$_4$ (II-E)**, or [11-methyl-13-(trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,12-dienato(1−)]nickel(II) tetrafluoroborate, was prepared by the same procedure except with the diketone 1,1,1-trifluoro-2,4-pentanedione and NaBF$_4$.[23] **Ni(Me$_2$[14]tetraenatoN$_4$) (III-G)**, or [5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato(2−)]nickel(II), was prepared by a multistep procedure from 3,3′-(ethylenebis(iminomethylidyne))-di-2,4-pentanedione and nickel(II) to form initially [6,13-diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato(2−)]nickel(II), which was deacetylated and demetalated to produce the macrocyclic ligand as the PF$_6^-$ salt followed by recomplexation with Ni(OAc)$_2$·4H$_2$O in the presence of NaOEt.[24b] **Ni(Me$_4$Bzo$_2$[14]hexaenatoN$_4$) (III-H)**, or [7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*]-1,4,8,11-tetraazacyclotetradecinato(2−)]nickel(II), was prepared as dark violet crystals from *o*-phenylenediamine and 2,4-pentanedione with Ni(OAc)$_2$·4H$_2$O in methanol.[25b] **Ni(Tfaced) (IV-J)**, or [1,1,1,1′,1′,1′-hexafluoro-4,4′-(ethane-1,2-diyldiimino)dipent-3-en-2-onato(2−)]nickel(II), was prepared from the preformed ligand derived from 1,1,1-trifluoro-2,4-pentanedione and 1,2-diaminoethane with Ni(OAc)$_2$·4H$_2$O.[26] **Ni(Aceted) (IV-K)**, or [2,2′-(ethylenebis(nitrilo-1-ethylidyne))diphenolato(2−)]nickel(II), was prepared by a similar procedure with *o*-hydroxyacetophenone.[27] **Ni(TPP) (V-L)**, or [5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato(2−)]nickel(II), was prepared from the free ligand (Aldrich) and Ni(OAc)$_2$·4H$_2$O in refluxing DMF.[28] **Ni(DMPE)(ClO$_4$)$_2$ (VI-M)**, or bis[1,2-bis(dimethylphosphino)ethane]nickel(II) perchlorate, was prepared from 1,2-bis(dimethylphosphino)ethane and Ni(ClO$_4$)$_2$ in methanol.[29] **Ni(DPHOS)$_2$(ClO$_4$)$_2$ (VI-N)**, or bis[*o*-phenylenebis(dimethylphosphine)]nickel(II) perchlorate, was prepared as bright yellow crystals from impure *o*-phenylenebis(dimethylphosphine) and Ni(ClO$_4$)$_2$.[9a] Treatment of this complex with sodium cyanide led to the pure ligand. **Ni(TfacDPT) (VII-Q)**, or [4,4′-[iminobis(3,1-propanediylnitrilo)]bis(1,1,1-trifluoro-2-pentanonato)(2−)]nickel(II), was prepared from the preformed ligand and Ni(OAc)$_2$·4H$_2$O in refluxing DMF.[30] **Ni(MeOBenzDPT) (VII-R)**, or [2,2′-[iminobis((3,1-propanediylnitrilo)phenylmethylidyne)]bis(5-methoxyphenolato)(2−)]nickel(II), was formed as green crystals from the preformed ligand and Ni(OAc)$_2$·4H$_2$O in ethanol with sodium ethoxide.[31]

Acetonitrile (2 L, Fisher, HPLC grade) was stirred with 25 g of solid KMnO$_4$ for 1 day, filtered, and distilled. The distilled acetonitrile was refluxed over P$_2$O$_5$ for ~15 h and distilled. Acetonitrile was finally refluxed over CaH$_2$ for ~15 h and distilled and stored under argon in Teflon-stoppered flasks. Dichloromethane (2 L, Fisher, certified ACS grade) was stirred with 100 mL of concentrated H$_2$SO$_4$ for 1 day. Dichloromethane was separated and washed with sodium carbonate solution and then with water. Dichloromethane was then refluxed over P$_2$O$_5$ for ~15 h and distilled. It was again refluxed over CaH$_2$ for ~15 h and distilled and stored under argon in Teflon-stoppered flasks.

Instrumentation. IR spectra were recorded on a Nicolet 10DX FT spectrometer. The electronic spectra were recorded on a Hewlett-Packard (HP) 8450 A diode array spectrometer. GC–MS analysis was carried out on an 18-m cross-linked dimethylsilicone capillary column fitted into a HP 5890 gas chromatograph that was interfaced to a HP 5970B mass spectrometer. ^{1}H NMR spectra were obtained on a JEOL FX-90Q FT spectrometer.

Catalytic Epoxidation of Olefins. All epoxidations were carried out under an argon atmosphere with anhydrous solvents. In a typical experiment, 1.0 × 10^{-2} mmol of the nickel(II) complex and 1 mmol of the olefin were added to 1 mL of the solvent followed by 0.01–0.03 mmol of iodosylbenzene. The course of reaction was monitored by periodically extracting an aliquot for GC–MS analysis of epoxide and iodobenzene. Authentic samples of epoxides and various side products were available from the previous studies.[3,7] Chlorobenzene was the internal standard of choice for olefin oxides except with cyclohexene, for which *n*-decane was used. In those experiments that used larger quantities of terminal oxidant, the typical quantities of the reagents were 1.0 × 10^{-2} mmol of nickel(II) catalyst and 0.15 mmol of iodosylbenzene in 5.0 mL of solvent.

Since the oxidations of (*E*)- and (*Z*)-β-methylstyrene afforded a particularly interesting complexion of products, they were analyzed in detail as follows. For (*Z*)-β-methylstyrene three experiments were carried out with various amounts of Et$_3$PO as an added donor. Thus, to a standard mixture containing 0.01 mmol of Ni(cyclam)(ClO$_4$)$_2$, 0.20 mmol of (*Z*)-β-methylstyrene, and 0.17 mmol of iodosylbenzene in 5 mL of dichloromethane was added (I) no Et$_3$PO, (II) 2 equiv of Et$_3$PO, and (III) 10 equiv of Et$_3$PO. The analysis (in μmol) of cis and trans epoxide, phenylacetone, β-phenylpropionaldehyde, benzaldehyde and iodobenzene a seriatim was followed periodically as follows. 30 min: (I) 1.3, 2.2, 0, 0, 1.0, 53; (II) 2.2, 4.3, 0, 0.5, 2.3, 121. 2 h: (I) 5.3, 4.0, 1.5, 0.4, 2.0, 80.8; (II) 10.9, 8.4, 2.8, 0.4, 3.7, 118; (III) 16.1, 11.7, 5.4, 0.8, 2.9, 191. 5 h: (I) 12.7, 6.9, 4.0, 0.8, 3.3, 145; (II) 29.3, 14.4, 9.8, 1.3, 4.1, 218; (III) 22.7, 14.3, 8.0, 1.0, 3.2, 220. 12 h: (I) 0.4, 0, 45.7, 2.7, 8.8, 188; (II) 23.4, 13.6, 9.6, 1.2, 4.0, 225; (III) 28.2, 10.1, 16.2, 1.7, 5.9, 221. Similarly, to a standard mixture containing 0.01 mmol of Ni(cyclam)(ClO$_4$)$_2$, 0.20 mmol of (*E*)-β-methylstyrene, and 0.17 mmol of iodosylbenzene in 5.0 mL of dichloromethane was added (IV) no Et$_3$PO, (V) 2 equiv of Et$_3$PO, (VI) 10 equiv of Et$_3$PO, (VII) 2 equiv of pyO, and (VIII) 10 equiv of pyO. The analysis (in μmol) of cis and trans epoxide, phenylacetone, β-phenylpropionaldehyde, and benzaldehyde a seriatim was followed periodically as follows. 2 h: (IV) 0, 14.4, 2.1, 0.3, 3.7; (V) 0.3, 24.3, 5.2, 0.5, 2.3; (VI) 0.4, 31.6, 6.9, 0.6, 2.8; (VII) 0, 32.5, 0, 0.3, 16.9; (VIII) 0, 21.2, 0, 0.3, 2.2. 48 h: (IV) 0, 0.5, 41.1, 1.8, 11.2; (V) 0.5, 26.6, 18.0, 1.3, 3.3; (VI) 0.5, 31.6, 15.1, 1.2, 3.4; (VII) 0.3, 43.8, –, 0.5, 23.7; (VIII) 0.2, 18.9, 4.6, 0.5, 2.8. The iodobenzene was not analyzed owing to problems with the complete chromatographic separation from (*E*)-β-methylstyrene.

Nickel Catalysis of Cyclohexane Oxidation. In a typical procedure a mixture of Ni(cyclam)(ClO$_4$)$_2$ (0.01 mmol), iodosylbenzene (0.15 mmol), and cyclohexane (0.3 mmol) in 5 mL of dichloromethane was stirred for 6 h. Analysis of the reaction mixture indicated that 0.10 mmol of iodobenzene was formed together with 7.9 × 10^{-3} mmol of cyclohexanone (8%) and 1.7 × 10^{-3} mmol of cyclohexanol (2%). When the amount of cyclohexane was increased to 9.0 mmol, the yield of cyclohexanone and cyclohexanol was essentially unchanged. The same results were obtained if 0.02 mmol of triethylphosphine oxide was present.

In a control experiment, 0.10 mmol of cyclohexanol was treated with 0.01 mmol of Ni(cyclam)(ClO$_4$)$_2$ and 0.02 mmol of iodosylbenzene in 1 mL of dichloromethane. After 6 h, a quantitative yield of iodobenzene was obtained together with 7.1 × 10^{-3} mmol (28%) of cyclohexanone. When the amount of cyclohexanol was doubled (0.20 mmol), the yield of cyclohexanol increased to 35%. Further addition of cyclohexanol (0.28 mmol) decreased the conversion of iodosylbenzene (76%) and concomitant reduction of cyclohexanone (25%). In the latter case, the reaction was unaffected by the presence of 2 equiv of triethylphosphine oxide.

Direct Reaction of Ni^{II}(cyclam)(ClO$_4$)$_2$ and Iodosylbenzene in the Absence of Hydrocarbon Substrates. Ni^{II}(cyclam)(ClO$_4$)$_2$ (0.01 mmol) in 1 mL of acetonitrile was prepared in four separate tubes to which 1, 2, 4, and 8 equiv of iodosylbenzene were added. The dissolution of PhIO occurred relatively readily (<10 min), with the exception of the eighth equivalent, which dissolved very slowly. To each was added 7 mL of diethyl ether. The brown precipitates were separated, and each was washed with diethyl ether and redissolved in acetonitrile. The UV–vis spectra of the first three samples showed a pair of weak bands at ~285 and 385 nm, which were both absent in the fourth sample. The IR spectrum of the solid from the reaction with 2 equiv of PhIO consisted of bands at 3220 (vs), 2959 (s, b), 2877 (w), 2363 (m), 2336 (m), 1647 (vs, b), 1540 (m), 1463 (m), 1435 (w), 1381 (w, b), 1316 (w, b), 1147 (s), 1114 (s), 1089 (s), 941 (m), 881 (w), 835 (w), 780 (m, b), 668 (m), 670 (s), and 627 (s) cm^{-1}.

The procedure to remove cyclam from Ni(cyclam)$^{2+}$ by treatment with refluxing aqueous NaCN[16b] was repeated. It indeed afforded the pure free ligand, the identity of which was confirmed by GC–MS and ^{1}H NMR analysis. By comparison the treatment of the recovered nickel complex was not as successful. For example, Ni(cyclam)(ClO$_4$)$_2$ (0.2 mmol) in 100 mL of MeCN was treated with 0.2 mmol of iodosylbenzene portionwise. The brown solid isolated as described above was dissolved in 50 mL of water and treated with 1.2 mmol of NaCN. However, the decomplexation occurred slowly. Thus after it was refluxed for 15 h, the solution was made alkaline with sodium hydroxide and then concentrated in vacuo. The mixture was repeatedly extracted with chloroform to yield only small quantities of a viscous oil, which could not be identified as a discrete compound.

Treatment of Ni(cyclam)$^{2+}$ with *m*-Chloroperbenzoic Acid. A suspension of Ni(cyclam)(ClO_4)$_2$ (0.05 mmol) in 30 mL of dichloromethane was cooled to −78 °C, and a solution of MCPBA (0.05 mmol) in 5 mL of dichloromethane was added slowly. The mixture was stirred at −78 °C for 1 h, during which the original orange-yellow color turned pink. When a solution of phenyldimethylphosphine (0.2 mmol) in dichloromethane was added, the pink color was discharged within 5 min. GC–MS analysis confirmed the formation of the phosphine oxide in >80% yield. When this experiment was repeated with cyclohexene, no change occurred at −78 °C. When the mixture was warmed to room temperature, it turned black and no oxidation product of cyclohexene was observed.

A yellow solution of Ni(cyclam)(OTf)$_2$ (0.02 mmol) in 4 mL of dichloromethane was cooled to −78 °C and the electronic spectrum recorded. A solution of MCPBA (0.02 mmol) in dichloromethane was added slowly and the spectrum of the pink solution recorded again (Figure 1). Upon the addition of PMe_2Ph, the absorption band at 550 nm disappeared, and the solution returned to its yellow color. When the experiment was repeated with cyclohexene, the band at 550 nm did not disappear.

An intensely green solution of Ni^{III}(cyclam)$^{3+}$ perchlorate[20] in acetonitrile reacted completely with excess iodosylbenzene within 2 min to lead to a yellow solution that contained a quantitative yield of iodobenzene. It is possible that iodosylbenzene is acting as a reducing agent under these conditions.

Isotopic Oxygen-18 Studies. Ni(cyclam)(ClO_4)$_2$ (0.01 mmol) and norbornene (1 mmol) were dissolved in 1 mL of MeCN, and $H_2{}^{18}O$ (1.85 mmol) was added together with 0.02 mmol of iodosylbenzene. After the mixture was stirred for 30 min, the norbornene oxide was analyzed by GC–MS for its isotopic composition. A control experiment was carried out in which norbornene oxide-^{16}O (1.0 mmol) was treated with $H_2{}^{18}O$ (1.85 mmol) in the presence of Ni(cyclam)(ClO_4)$_2$ (0.01 mmol) and iodosylbenzene (0.02 mmol) in 1 mL of MeCN. The recovered epoxide showed no isotopic incorporation. Moreover, the treatment of iodosylbenzene (0.05 mmol) with $H_2{}^{18}O$ (2 mmol) in the presence of Ni(cyclam)(ClO_4)$_2$ (0.01 mmol) was carried out until half of it was in solution. The remainder of the iodosylbenzene was recovered. Analysis by a procedure developed previously[3,7] showed that it contained no isotopic label.

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New, One-Step Syntheses of BrF_3O and BrF_4O^- Salts and the Preparation and Characterization of $RbBrF_4O$ and $NaBrF_4O$

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The reactions of an excess of BrF_5 with the alkali-metal nitrates $NaNO_3$, KNO_3, $RbNO_3$, and $CsNO_3$ provide new, simple, high-yield syntheses of the corresponding BrF_4O^- salts and FNO_2. The $NaBrF_4O$ and $RbBrF_4O$ salts have been prepared for the first time and were characterized by vibrational spectroscopy, DSC, and their X-ray powder diffraction patterns. The reaction of $LiNO_3$ with an excess of BrF_5 does not result in the formation of a stable $LiBrF_4O$ salt but produces free BrF_3O in high yield. This provides a simple, one-step synthesis of BrF_3O from commercially available starting materials.

Introduction

The existence of $KBrF_4O$ was discovered in 1976 both by Bougon and co-workers[1] and by Gillespie and Spekkens.[2] It was prepared either by the reaction[1] of $KBrO_3$ with a large excess of BrF_5 at 80 °C in the presence of F_2 or by the reaction[2] of $KBrF_6$ with $KBrO_3$ in CH_3CN solution. Both methods have drawbacks. Although Bougon's method[1] can yield a pure product, the course of the reaction is difficult to control and frequently $KBrF_4$ is obtained as the only product,[3] Gillespie's method[2] produces a mixture of $KBrF_2O_2$ and $KBrF_4O$, which must be separated by numerous extractions with CH_3CN.

An improved synthesis of BrF_4O^- salts was reported by Christe and co-workers[3] who reacted BrO_4^- salts with BrF_5 and F_2. In addition to $KBrF_4O$, the latter authors also prepared and characterized $CsBrF_4O$. Although this method results in a pure product in essentially quantitative yield,[3] the required BrO_4^- starting materials are difficult to prepare.[4] Except for $NF_4^+BrF_4O^-$,[5] no other BrF_4O^- salts have been reported.

Three methods have previously been reported for the synthesis of BrF_3O. Bougon and Bui Huy[6] reacted $KBrF_4O$ with O_2AsF_6 in BrF_5 solution.

$$KBrF_4O + O_2AsF_6 \rightarrow KAsF_6 + BrF_3O + O_2 + {}^1/{}_2F_2 \qquad (1)$$

Gillespie and Spekkens[2] dissolved $KBrF_4O$ in anhydrous HF

$$KBrF_4O + HF \rightleftarrows KHF_2 + BrF_3O \qquad (2)$$

and extracted the formed BrF_3O with BrF_5 at low temperature. Adelhelm and Jacob[7] obtained BrF_3O, together with $FBrO_2$, by treatment of a mixture of BrF_2OPtF_6 and BrO_2PtF_6 with FNO_2.

$$BrF_2OPtF_6 + FNO_2 \rightarrow NO_2PtF_6 + BrF_3O \qquad (3)$$

$$BrO_2PtF_6 + FNO_2 \rightarrow NO_2PtF_6 + FBrO_2 \qquad (4)$$

All three methods are elaborate and involve several steps and exotic starting materials. The development of a new, simple, one-step synthesis of BrF_3O from commerically available starting materials was therefore highly desirable.

Experimental Section

Materials. Commercial $LiNO_3$ (J. T. Baker, 99.7%), $NaNO_3$ (J. T. Baker, 99.5%), KNO_3 (J. T. Baker, 99.1%), and $RbNO_3$ (K & K Labs, Inc., 99.9%) were dried in a vacuum oven at 120 °C for one day prior to their use. The $CsNO_3$ was prepared from Cs_2CO_3 and HNO_3 and dried in the same manner. The BrF_5 (Matheson) was treated with 35 atm of F_2 at 100 °C for 24 h and then purified by fractional condensation through traps kept at −64 and −95 °C, with the material retained at −95 °C being used. BrF_5 and BrF_3O are powerful oxidizers, and contact with organic materials or moisture must be avoided.

Apparatus. Volatile materials used in this work were handled in a well-passivated (with BrF_5 until it was recovered as a white solid at −196

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