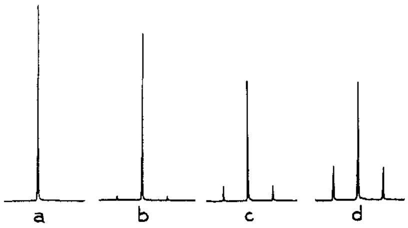

Figure 1. Aldehyde proton resonance (400 MHz) for $RhCl(CO)(PPh_3)_2$ + ^{13}CO + PhCHO in C_6D_6 showing successive incorporation of ^{13}C isotope into benzaldehyde. The resonance is at δ 9.63 ppm with $J(^{13}C\text{-}H)$ of 173 Hz. Irradiation times: (a) $t = 0$; (b) 1 day; (c) 5 days; (d) 10 days.

which we calculate $\Delta G°_{298} = +1.7$ kcal.[9] The reverse reaction, PhCHO decarbonylation, has been studed in detail by others.[10] As a catalytic reaction using $RhCl(CO)(PPh_3)_2$, it is found to require temperatures greater than 170 °C. In contrast, we find that $RhCl(CO)(PPh_3)_2$ is a photochemical decarbonylation catalyst at ambient temperature, as shown by photolysis of a 7.2 mM solution of $RhCl(CO)(PPh_3)_2$ (4 μmol) containing 20 μmol of PhCHO. After 24 h of photolysis, the amount of PhCHO had decreased to 12 μmol as determined by GC analysis. In an earlier report, Geoffroy et al. observed that treatment of photolyzed solutions of $RhCl(CO)(PPh_3)_2$ with PhCHO led to benzene formation, but they did not see direct photochemical decarbonylation using heptanal as substrate.[11]

In order to confirm that the low yields of PhCHO produced in the photolysis of benzene solutions of $RhCl(CO)(PPh_3)_2$ were indeed the result of thermodynamic limitations and not kinetic inactivity of the system, an experiment was performed using ^{13}CO. A benzene-d_6 solution containing 3.0 mg of $RhCl(CO)(PPh_3)_2$ (4.3 μmol) and 2.0 μL of PhCHO (19.6 μmol) was placed under 1.2 atm of ^{13}CO and irradiated at 22 °C through a Pyrex filter. Examination of the aldehyde resonance by ^1H NMR (δ 9.63, $J_{C\text{-}H} = 173$ Hz) revealed significant incorporation of ^{13}CO into benzaldehyde, confirming the occurrence of carbonylation/decarbonylation sequences. As shown in Figure 1, the ^{13}C satellites of the aldehyde proton showed a steady increase in intensity over 10 days at which time the extent of ^{13}CO incorporation into PhCHO amounted to 38%. During this period, the PhCHO concentration decreased from 36 mM (5 equiv) to 21 mM (2.9 equiv) as determined by GC analysis.[8]

While this demonstrates the reversibility of photochemical carbonylation, it raises the question of whether there is a common intermediate for both the forward and reverse reactions or a photostationary state resulting from two independent photoreactions. To test this, three identical samples were prepared (7.5 mM complex, 12 mM PhCHO, and 1.0 atm of CO) and irradiated through a Pyrex filter for 3 days. One tube was opened and GC analysis showed that the PhCHO concentration had decreased to 10.5 mM. The other two samples were placed at distances 4 and 16 cm from the light source and irradiated for another day. Analysis of these two samples showed each to be 10.1 mM in PhCHO, indicating that carbonylation and decarbonylation proceed through a common intermediate and result eventually in an equilibrium mixture of PhCHO, CO, and benzene.

To account for the incorporation of ^{13}CO into PhCHO under photolysis, equivalence of ^{12}CO and ^{13}CO is required at some point in the catalysis. This may be achieved via free CO in solution or a dicarbonyl intermediate. The pathways leading to photochemical carbonylation and decarbonylation involve the same initial step which we believe is loss of a ligand to generate a 14-e$^-$ intermediate. While Ford and Wink have demonstrated efficient photochemical dissociation of CO from $MCl(CO)(PPh_3)_2$, they see no net reaction chemistry under the conditions of their experiment.[1,2] The formation of benzaldehyde in the present study may result from either a relatively inefficient reaction of $MCl(PPh_3)_2$ with C_6H_6 leading to arene activation and carbonylation, or from a second photochemical process which occurs much less efficiently than CO photodissociation. This process could be phosphine dissociation to generate $MCl(CO)(PPh_3)$.

Support for the notion of ligand dissociation as the photochemical step is obtained from photolyses carried out under different CO pressures and in the presence of added phosphine. Two 7.5 mM benzene solutions of $RhCl(CO)(PPh_3)_2$ under 36 and 615 mm of CO were prepared. The samples were irradiated and monitored by ^1H NMR spectroscopy[7b] for 20 h. Analysis by GC showed the samples to be 4.1 and 1.8 mM, respectively, in benzaldehyde. Thus the efficiency of benzene carbonylation is reduced as CO pressure is increased. The addition of PPh_3 to a benzene solution of $RhCl(CO)(PPh_3)_2$ under CO causes rapid formation of $RhCl(PPh_3)_3$ upon irradiation in accord with the results of Ford[1] and inhibition of benzaldehyde formation.

While further mechanistic details remain to be elucidated, the key point of the present study is that Rh(I) and Ir(I) phosphine complexes do exhibit photochemical reactivity which leads to significant, new reaction chemistry. If the arene carbonylation reaction seen here can be driven to overcome its unfavorable thermodynamics such as by subsequent hydrogenation, this photochemical functionalization may prove useful as well as interesting.

Acknowledgment. We thank the National Science Foundation (CHE 83-08064) for support of this work, and the Johnson Matthey Co., Inc., for a generous loan of rhodium salts. We also thank Prof. Jack Kampmeier and Tong-Zhou Liu for helpful discussions and Dr. Romana Lashewycz-Rubycz for experimental assistance.

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Sustained Epoxidation of Olefins by Oxygen Donors Catalyzed by Transition Metal Substituted Polyoxometalates, Oxidatively Resistant Inorganic Analogues of Metalloporphyrins

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Received July 1, 1985

The homogeneous catalytic oxygenation of saturated and unsaturated hydrocarbons has been one of the most active areas of chemical research in the last 5 years.[1-12] Numerous metallo-

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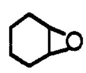
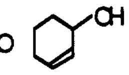
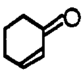
porphyrin-based systems for the catalytic epoxidation of olefins using sources of reduced oxygen such as iodosylbenzene, hypochlorite, amine *N*-oxides, hydrogen/Pt plus oxygen, and others have been described recently.[3-10] The investigation of these systems has furthered substantially our understanding not only of the mechanism of action of cytochrome P-450 and other heme enzymes but also of homogeneous oxygenation and atom-transfer oxidation processes in general. A major obstacle in the development of metalloporphyrin-catalyzed oxidation processes into practical oxidation processes, however, is the instability of porphyrin catalysts. The substitution of bulky groups into the ortho positions of tetraarylporphyrins has recently been shown to increase greatly the stability of the corresponding metalloporphyrins with regard to oxidative degradation,[4b,10] but porphyrins are, nevertheless, organic molecules and inherently unstable thermodynamically in the presence of strong oxidizing agents. As a consequence, all metalloporphyrins succumb eventually to oxidative degradation when used as hydrocarbon oxidation catalysts. Some transition-metal-substituted bleomycins[11] and transition-metal salts[12] catalyze the epoxidation of olefins by iodosylbenzene establishing that the presence of a porphyrin ligand is not essential for such atom-transfer oxidation processes.

We report here that the transition metal substituted heteropolytungstates of C_s point group symmetry, $(n\text{-Bu}_4\text{N})_4\text{H(M)PW}_{11}\text{O}_{39}$, M = transition metal, **1**-M, an accessible and soluble class of inorganic complexes,[13-15] are, for M = Mn^{II} and Co^{II}, remarkably effective catalysts for atom-transfer oxidation from oxygen donors including aniline *N*-oxide and iodosylarenes. Here we specifically address the homogeneous catalytic epoxidation of olefins by **1**-Mn and **1**-Co using iodosylbenzene (PhIO)[16] or pentafluoroiodosylbenzene (PFIB)[17] as oxygen donors. The product selectivities, reaction rates, and, most importantly, stabilities for these epoxidations compare favorably with those for all metalloporphyrin and related systems in the literature. The complexes, **1**-M, are not as susceptible to oxidative degradation during epoxidations as metalloporphyrins nor susceptible to inactivation by aggregation or other effects. Both complexes **1** and metalloporphyrins have high thermal stability and a well-defined active site situated in a ligand environment that is fairly rigid and chemically robust and exhibits a capacity for storing electrons. The transition metal active sites in complexes **1**, unlike those in metalloporphyrins, however, reside in a completely inorganic ligand environment containing only oxidatively stable oxide and d^0 W^{VI} ions.

Table I. Epoxidation of Olefins by Iodosylbenzene (PhIO) and Pentafluoroiodosylbenzene (PFIB) Catalyzed by Transition-Metal-Substituted Heteropolytungstates and Other Transition-Metal-Based Catalysts[a]

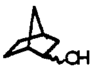
A. Cyclohexene oxidation

		Products (Yields, %)^{b,c}			
Catalyst^{d}	Oxidant				Aryl Iodide
1-Mn	PhIO	67	<1	2.5	72
1-Mn	PFIB	41	1.1	3.0	90
Mn(OTf)_2	PhIO	24	1.1	1.8	68
Mn(OTf)_2	PFIB	14	1.3	2.4	90
1-Co	PhIO	82	<1	2.0	76
Co(OTf)_2	PhIO	17	1.2	1.4	59
1-Fe	PhIO	no reaction			
1-Fe	PFIB	14	e	e	58
MnTPPCl	PhIO	24	6	3	70
FeTPPCl	PhIO	50	12	3	98
CoTPPCl	PhIO	e	<2	e	e

B. 1-Hexene oxidation

					Aryl iodide
					
1-Mn	PhIO	58	<<1	3.5	81
1-Mn	PFIB	55	<1	4	96
Mn(OTf)_2	PhIO	18	?	<1	77
Mn(OTf)_2	PFIB	24	2	10	80
FeTPPCl	PhIO	28	9	7	77
FeTPPCl	PFIB	11	3	3	90
FeTDCPPCl	PhIO	65	?	14	96
FeTDCPPCl	PFIB	76	5	16	98

C. Norbornene oxidation

					Aryl Iodide
1-Co	PhIO	96^{f}	e	e	97
Co(OTf)_2	PhIO	96^{f}	e	e	60

C. Cyclooctene oxidation^{g}

			Aryl Iodide
1-Co	PhIO	91	60
Co(OTf)_2	PhIO	25	54

[a] All reactions run with an olefin:oxidant:catalyst mol ratio of 500:10:1 at 24 °C under nitrogen or argon; solvent for metalloporphyrin reactions was CH_2Cl_2, solvent for all other reactions was CH_3CN; reaction times were 2 h for all PhIO reactions and 5 min for PFIB reactions; products identified and quantitated by GC and GC/MS analysis. [b] Yields of aryl iodide based on iodosylarene added; other yields based on oxidant consumed. [c] Yields of allylic alcohol were low and variable in all cases due to rapid subsequent oxidation. [d] Abbreviations: OTf = triflate, TPP = tetraphenylporphyrin dianion, TDCPP = tetrakis(2,6-dichlorophenyl)porphyrin dianion. [e] Below detectable limit (<0.1%). [f] Approximately 3% *endo*-epoxide present. [g] Yields of other products not determined.

Many epoxidation reactions by PhIO and PFIB catalyzed by **1**-Co and **1**-Mn as well as by metalloporphyrins and metal triflates have been extensively examined in our laboratory. Direct comparisons can be made between the **1**-M/PFIB systems and the [tetrakis(2,6-dichlorophenyl)porphinato]iron(III)/PFIB system examined by Traylor, Dolphin, and Traylor which exhibits rates, epoxide selectivites, and catalyst stability as high as any metalloporphyrin-based system in the literature.[4b] Representative reactions under low to moderate turnover conditions are summarized

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(15) The specific complexes, **1**-M, used as catalysts in this work, were prepared by metathesis of $\text{Na}_5\text{(M)PW}_{11}\text{O}_{39}$ with $(n\text{-Bu}_4\text{N})\text{Br}$ in water. Multiple recrystallizations from acetonitrile yielded the $(n\text{-Bu}_4\text{N})_4\text{H(M)PW}_{11}\text{O}_{39}$ compounds.

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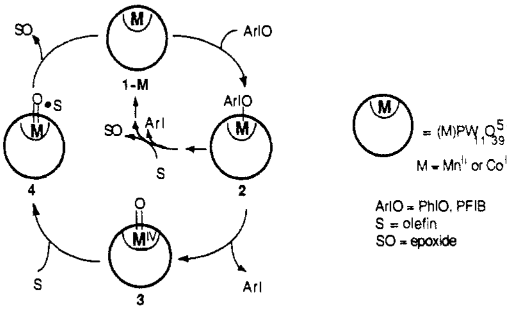
Scheme I



in Table I; exact reaction conditions are given in the table.[18] The following points pertain to all reactions catalyzed by **1**-M: (1) no reaction is seen in the absence of either **1**-M or oxidant; (2) the reactivity order for **1**-M is M = Mn^{II} and Co^{II} (most reactive) > Cu^{II} > Fe^{II} ~ Cr^{III} (almost inactive at 25 °C); (3) *trans*-stilbene gives *trans*-stilbene oxide and benzaldehyde only (6:1 mol ratio); *cis*-stilbene gives partially isomerized olefin, *cis*- and *trans*-epoxides, and benzaldehyde, products compatible with one or more freely rotating radical intermediates; (4) the selectivity for production of epoxide is higher in the reactions catalyzed by **1**-M than in the reactions catalyzed by the metal triflates or metalloporphyrins (>90% for **1**-M with all olefins examined);[18] (5) intermediate alkyl radicals are sufficiently long-lived and kinetically accessible to be scavenged by any dioxygen purposely added to the system producing typical autoxidation products (primarily allylic alcohol and allylic ketone vs. epoxide) but not by alkylated phenols, e.g., BHT; (6) the rates of epoxidation with PFIB, chosen as oxygen donor for its reactivity, follow the order **1**-Co and **1**-Mn (most reactive) ≥ FeTDCPPCl > MTPPCl > $M(OTf)_2$,[19] M = Fe^{III} or Mn^{III}; (7) most importantly, epoxidations catalyzed by **1**-M continue far longer than for all other systems examined. Several epoxidations with all the catalysts in Table I and PFIB were examined under high turnover conditions (10 000 equiv of PFIB per equiv of catalyst). The stability order of these homogeneous catalysts, monitored by both the spectral properties of the catalysts and the rate of PFIB uptake with time, is clear: $M(OTf)_2$ (least stable) < MTPPCl, M = Fe^{III} or Mn^{III}, ≪ FeTDCPPCl < **1**-M, M = Co^{II} or Mn^{II} (most stable). Only the catalysts, **1**-M, appear to be oxidatively stable in the absence of olefin substrate.

It is clear from monitoring the electronic spectra of the epoxidations catalyzed by **1**-Co or **1**-Mn that the Mn ion undergoes redox changes during catalysis, while the Co atom may not. These observations coupled with the known difficulty of obtaining Co in the 4+ oxidation state favors paths involving high-valent Mn species (e.g., oxomanganese (IV), **3** in Scheme I) in the processes catalyzed by **1**-Mn but paths not involving oxocobalt species (i.e., **1**-M → **2** → **1**-M in Scheme I) in the processes catalyzed by **1**-Co.

Studies are in progress that address the energetic and mechanistic features of these sustained epoxidation processes. At this stage it is apparent that **1**-M and related species may combine the stability of heterogeneous inorganic oxidation catalysts such as metal oxides with the experimental tractability of homogeneous oxidation catalysts containing organic ligands such as metalloporphyrins.

Acknowledgment. Support of this research by the National Science Foundation (Grant CHE-8402994) is acknowledged. We thank Judy Sophianopoulos for GC/MS analyses and Michael M. Williamson for the sample of FeTDCPPCl.

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[18] Reaction rates and catalyst stabilities were monitored directly and most effectively by gravimetric analysis of unreacted iodosylarene and by gas chromatographic analysis of iodoarene. Selectivities are defined as yield of epoxide/total yields of other volatile or chromatographically detectable products. Product mixtures were not analyzed for carboxylates or other nonvolatile materials which may be present.

[19] Abbreviations in Table I.

Enthalpies of Intramolecular Etheration of Saturated Organolithium Compounds in Benzene

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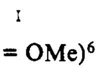
Received September 16, 1985

Data on alkyllithium–Lewis base (B) interaction obtained so far[1–5] pertain to *mixtures* of rapidly equilibrating complexes $R_4Li_4B_n$ (n = 1–4) and B and, consequently, depend upon concentrations and on the ratio RLi:B. For primary alkyllithiums, the gross calorimetric[3,4] and thermodynamic[5] data cannot be dissected into the separate contributions of the (free) energy of transfer of RLi from the hexameric state (predominating in hydrocarbons) to the tetrameric state (prevailing in solutions when the mole ratio of B to n-alkyllithium hexamer is about 1)[2b] and the (free) energy of complexation in the latter. In order to obtain data on specific complexes we have studied the lithium compounds I,[6] II,[7] III[7,8] and IV.[7] I and II crystallize as V (α-C = $CHCH_3$, Y = OMe)[6] and VI (α-C = CH_2, Y = OMe).[9] In hydrocarbon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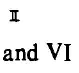
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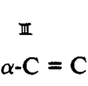
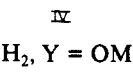

III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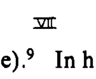
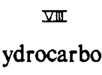
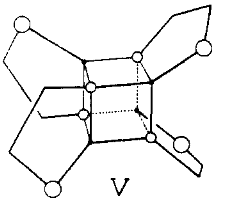
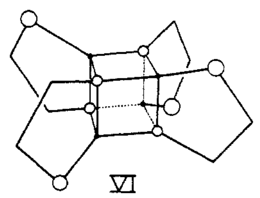

VII


VIII

O-Y o-α-C ..Li


V


VI

solutions VII is present as V (α-C = CH_2, Y = OMe) exclusively, as indicated by molecular weight and diastereotopic C-methyl groups and CH_2Li protons,[10] while VIII occurs as a mixture of V (α-C = CH_2, Y = NMe_2) and VI (α-C = CH_2, Y = NMe_2).[11] By analogy complexes V and/or VI most likely are the exclusive species present in hydrocarbon solutions of I–IV.[12,13] They are taken as models for corresponding, more ephemeral, intermolecular complexes $R_4Li_4(OR'_2)_4$.

Heats of reaction [$\Delta H_{r,s\text{-BuOH}}$(25 °C)] of ca. 10^{-3} M benzene solutions of I–IV and of the methoxy-free reference compounds

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[3] Quirk, R. P.; Kester, D. E. *J. Organomet. Chem.* **1977**, *127*, 111.

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[12] Since several diastereomeric tetramers seem to be present, unequivocal interpretation of the temperature-dependent NMR spectra of I has not yet been possible. The NMR spectra of II suggest the exclusive presence of tetramers of type VI.

0002-7863/86/1508-0538$01.50/0