(whose structure is as yet unspecified). If C came from the second intermediate and P from the first, then [P]/[C] would have been directly proportional to [A], contrary to the observation.

We originally thought that the second intermediate was the triplet carbene.[4] In related work on the reaction of diphenylcarbene with dichloroethene, we concluded that the singlet and triplet forms are almost certainly the respective product-forming intermediates leading to the structures analogous to C and P.[9] In the present case, however, there is a marked dependence of the product ratio [P]/[C] on the concentration of the starting mercury compound, $PhHgCBr_3$ (M). Since the initial decomposition of M to form the carbene precedes the branching point to the two intermediates, the ratio should have been independent of [M]. Even if M went directly to the two intermediates, there should be no dependence.[7] The single $\rightleftharpoons$ triplet interconversion should be fast and independent of [M]. *A detailed study of the kinetics revealed a first-order dependence of* [*P*]/[*C*] *on* [*M*]. Such a kinetic result requires the intervention of an additional molecule of M during the conversion of the singlet carbene to the second intermediate. The ratio [P]/[C] did not depend on the concentration of PhHgBr, which is poorly soluble in benzene. The combined dependence of [P]/[C] on [M] and 1/[A] (eq 2) is

$$\frac{[P]}{[C]} = \frac{k_2[M]}{k_3[A]} \qquad (2)$$

consistent with the mechanism in Scheme I.

Although the kinetics demand the existence of both free and complexed carbene, the events after the formation of the second intermediate are not well-defined. A possible structure of the metal–carbene complex is $(Ph)(CBr_3)Hg^+—\bar{C}Br_2 \leftrightarrow (Ph)(CBr_3)Hg{=}CBr_2$.[1,10] Reaction with the alkene could give a metallacyclobutane or its open-chain analogue, $(Ph)(CBr_3)Hg^+CBr_2CHCl\bar{C}HCl$.[11] Loss of the molecule of $PhHgCBr_3$ then produces the dipolar intermediate $^+CBr^2CHCl\bar{C}HCl$, of which the diradical D is a resonance structure. Because the second molecule of M is regenerated, it has served in a homogeneous catalytic role in the production of P.[12] These suggestions at present are hypothetical.

The low reactivity of dichloroethene is the key to the entire mechanistic scenario. Its poor reactivity with the electrophilic singlet carbene in the metal-free system[9] permits intersystem crossing to the triplet and formation of the rearranged propene. More reactive alkenes such as the 2-butenes would have led solely to the stereospecific cyclopropane via the singlet as the only intermediate.[13,14] In the presence of the metal (M), the carbene forms a more nucleophilic intermediate by complexation rather than by intersystem crossing. This complex then reacts more readily with the weak substrate, dichloroethene. This pathway leads to chlorine migration and to the product P.

In summary, we have observed kinetic evidence that requires an interconversion between dibromocarbene and its complex with $PhHgCBr_3$.[15] The free carbene reacts with the alkene to form the cyclopropane C. The complexed carbene leads to the rearranged propene P. The primary function of the complexing $PhHgCBr_3$ is to heighten the reactivity of the carbene with the relatively unreactive dichloroethene. These results suggest numerous experiments with other carbenes, other alkenes, and other metallic complexing agents, which we currently are prosecuting.

Acknowledgments. We are indebted to Professors Frederick D. Lewis, Tobin J. Marks (both of Northwestern University), M. Jones, Jr. (Princeton), and Keiji Kobayashi (University of Tokyo) for comments and suggestions during this research. We thank the National Science Foundation for support of this work through Grant CHE79-05542.

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(9) Gaspar, P. P.; Whitsel, B. L.; Jones, M., Jr.; Lambert, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 6108.

(10) Mercury–carbene complexes are not common, but some have been suggested: Wanzlick, H.-W.; Schönherr, H.-J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141–142. Schöllkopf, U.; Gerhart, F. *Ibid.* **1967**, *6*, 560–561, 970, 805.

(11) The formation of the metallacycle might imply the production of some $CHCl{=}CBr_2$ or adducts of CHCl, which we have not as yet found.

(12) It should be emphasized that the second molecule of $PhHgCBr_3$ is not unique in fulfilling this role. The first molecule is necessary to produce CBr_2. The second molecule, in its complexation role, can be replaced by other materials. We have found that other PhHgR compounds, which do not produce a carbene, in the presence of decomposing $PhHgCBr_3$ strongly affect [P]/[C].

(13) The reaction of CBr_2 with the 2-butenes is stereospecific and without rearrangement: Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, *78*, 3409–3411.

(14) The low reactivity of dichloroethene has frustrated the realization of one obvious experiment, the production of CBr_2 from a nonmetallic source. We have generated CBr_2 by all the common procedures, without observing any reaction with this alkene. Apparently, other components of the mixture ($CHBr_3$, protic solvent, etc.) intercept the carbene before it can react with dichloroethene.

(15) These studies confirm Seyferth's original mechanism of cyclopropane formation from a free carbene: Seyferth, D.; Mui, J. Y.-P.; Burlitch, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 4953–4959. Our additional conclusions all derive from the rearranged propene product that was previously not of interest.

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Cobalt–Nitro Complexes as Oxygen Transfer Agents: Oxidation of Olefins

Sir:

Recently, the need has been emphasized for developing nonradical systems for specific oxidation of organic substrates by molecular oxygen.[1] Previously, we have offered a novel appraoch consisting of oxygen transfer from the nitro ligand of metal–nitro complexes to organic substrates accompanied by the formation of the corresponding nitrosyl complexes. The catalytic cycle is then completed by reoxidation of the nitrosyl ligand by molecular oxygen.[2] Using $py{\cdot}Co(saloph){\cdot}NO_2$ (I) (saloph = *N*,*N*′-bis(alicylidene-*o*-phenylene)diamino), we have demonstrated oxidation of phosphines to phosphine oxides and oxomolybdenum(IV) complexes to dioxomolybdenum(VI) species.[2] Interaction of the nitro ligand in I and in $py{\cdot}Co(TPP){\cdot}NO_2$ (II) (TPP = tetraphenylporphyrin) with Lewis acids [e.g., BF_3, Li^+] enhances its electrophilicity and thus its oxidation power. This combination of cobalt–nitro complexes with Lewis acids extended this oxidation chemistry to organic sulfides, alcohols, and 1,3-cyclohexadiene,[3] but not to monoolefins. We now report a system which represents an important modification of the above concept. It enables us to employ cobalt–nitro complexes as stoichiometric oxidants and as catalysts for the oxidation of monoolefins.

Cobalt–Nitro Complexes as Oxygen Transfer Agents. The nitro ligand in I and II can formally be regarded as a nitrogen-bound monoanionic ligand ($Co^+{-}NO_2^-$), and as such it may function as a weak, oxygen-centered nucleophile. We have attempted to use this property of the nitro ligand and activate olefins toward a nucleophilic attack by coordinating them to higher valent group 8 metals such as palladium(II).[4] Initially, we concentrated our

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(1) More than 50% of the chemicals needed in industry are prepared by oxidation of petrochemicals. Due to the change in price and availability of the petrochemicals, novel, specific oxidation processes are needed. "Selective Catalytic Oxidation of Hydrocarbons: A Critical Analysis". Catalytica Associates, Inc., Santa Clara, CA, Multiclient Study No. 1077, October 1979.

(2) Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am. Chem. Soc.* **1979**, *101*, 270.

(3) Tovrog, B. S.; Diamond, S. E.; Mares, F.; Szalkiewicz, A., submitted; presented in part at the 177th National Meeting of the American Chemical Society, Honolulu, HI, April 1979, and at the First International Symposium on Activation of Molecular Oxygen and Selective Oxidations Catalyzed by Transition Metal Complexes, Bendor, France, May 1979.

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Table I. Stoichiometric Oxidation of Olefins by Cobalt–Nitro Complexes[a]

run	complex	molar ratio Pd/Co	solvent	time, min	product yield,[b] %
	ethylene				acetaldehyde
1	I + IV	1.53	DCE	70	100
2		1.92	THF	55	100
3	II + IV	1.84	DCE	70	73
4		2.57	THF	120	100
5	IV[c]		DCE	90	0
6	I[d]		DCE	90	0
					vinyl acetate
7	I + $Pd(OAc)_2$	0.99	AcOH	300	100[e]
	propylene				acetone
8	II + IV	2.39	diglyme	190	100

[a] The oxidations were run under 1 atm of olefin, at 50 °C, using a 10 mM solution of I or II in deoxygenated and dried solvents. The nitro complexes I or II are cleanly reduced to the nitrosyl complexes Ia or IIa. No palladium metal is formed unless stated otherwise. [b] Based on I or II. [c] A 10.2 mM solution of IV was used. [d] The nitro complex I was isolated unchanged. [e] The yield of vinyl acetate is based on the total amount of I and $Pd(OAc)_2$. Palladium metal precipitates.

efforts on ethylene oxidation with $[(C_2H_4)PdCl_2]_2$ (III) prepared in situ from $(PhCN)_2PdCl_2$ (IV) and ethylene.[5] Thus, at 50 °C under 1 atm of oxygen-free ethylene, in *dried* and deoxygenated solvents [e.g., 1,2-dichloroethane (DCE), THF, or diglyme), a reaction of III with I produced acetaldehyde in 100% yield,[6] based on I (Table I, runs 1 and 2). The nitro complex I is quantitatively and cleanly reduced to the corresponding nitrosyl complex, Co(saloph)·NO (Ia).[7] There is no evidence of palladium metal in the reaction solution. The original divalent state of palladium may be verified by subsequent addition of *deoxygenated* acetic acid. This results in the formation of vinyl acetate, the typical Wacker product, in 94% yield, based on IV originally added to the reaction mixture. Control experiments (Table I, runs 5 and 6) (a) I with ethylene and (b) IV with ethylene gave no products, demonstrating that the cobalt–nitro complex/palladium(II) combination is essential for acetaldehyde formation. Under the reaction conditions, in the presence of IV together with I or Ia, ethylene oxide shows no measurable isomerization to acetaldehyde. Thus, acetaldehyde is the primary product of the oxidation. When propylene is used as the substrate, the oxidation yields acetone quantitatively (Table I, run 8) with no evidence of propionaldehyde, acrolein, or propylene oxide. The generality of the oxidation is suggested by the observations that the reactivity of I and II is similar (Table I); both ethylene and propylene can be oxidized, and different nonnucleophilic solvents can be employed. All the data accumulated so far demand that the oxygen in acetaldehyde or in acetone originates from the nitro ligand of I or II, demonstrating *the oxygen transfer nature* of this novel oxidation.

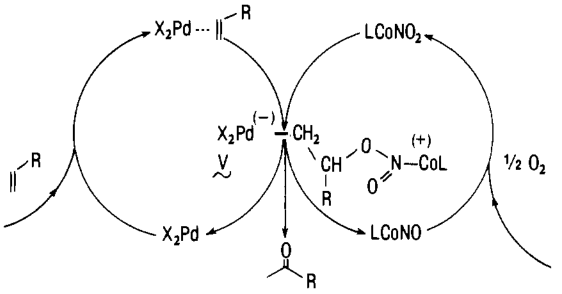
The ability of cobalt–nitrosyl complexes to be reoxidized by molecular oxygen has previously allowed us to convert stoichiometric oxidations by cobalt–nitro complexes into catalytic reactions employing dioxygen as the oxidant.[2,3] The data in Table II show that the combination of cobalt–nitrosyl or cobalt–nitro complexes with palladium(II) does catalyze oxidation of ethylene to acetaldehyde. The rate of the aldehyde formation appears to be linear with time (Table II, runs 3 and 4). The activity of I and II is comparable, in agreement with the stoichiometric oxidations. In all the catalytic oxidations, aliquots were withdrawn at various time intervals, and the cobalt complexes were isolated and shown to be present predominantly as nitrosyl complexes.[7] Thus, at least in an oxygen-lean atmosphere, the reoxidation of the nitrosyl to nitro ligand seems to be the rate-determining step. At atmospheric pressure in an oxygen-rich atmosphere (Table II, run 2), the oxidations give inferior results, likely due to the inability of IV to complex ethylene at such a low partial pressure (~0.05 atm).

Table II. Olefin Oxidation by Molecular Oxygen Catalyzed by Cobalt–Nitro Complexes[a]

run	complex	molar ratio Pd/Co	solvent	time, min	mol of product/ mol of Co
	ethylene				acetaldehyde
1	I	2.42	diglyme	240	3.2
2		2.10	THF	360	1.0[b]
3		2.32	DMF	120	4.1
				240	8.4
4	II	3.09	diglyme	120	2.3
				240	4.8
				360	6.8
5	IIa	2.40	diglyme	120	6.0
				240	12.2
					vinyl acetate[c]
6	I	3.61	AcOH	240	5.4
7	II	3.47	AcOH	120	3.6
				240	7.4
				480	12.8
8	$Pd(OAc)_2$		AcOH	420	0.89[d]
	propylene				acetone[e]
9	II	2.56	diglyme	480	1.7

[a] The oxidations were run at 70 °C, 1 atm pressure, with gas bubbled through a 10 mM solution of I or II in dried solvent with IV as cocatalyst unless stated otherwise. The gas flow was 24 mL/min of olefin and 4 mL/min of O_2 unless stated otherwise. The products were trapped from the exit gases in THF at -77 °C (acetaldehyde and acetone) or in toluene at -10 °C (vinyl acetate). [b] The gas flows were 3 mL/min of ethylene, 15 mL/min of O_2, and 10 mL/min of Ar. [c] IV was replaced by $Pd(OAc)_2$ in all oxidations carried out in acetic acid. [d] Only $Pd(OAc)_2$ (10 mM solution) and no nitro–coblat complex were present in the reaction mixture. The yield is based on $Pd(OAc)_2$. Palladium metal was formed. [e] The gas flows were 18 mL/min of propylene and 16 mL/min of O_2.

Scheme I



All the results obtained in stoichiometric as well as in catalytic oxidations are consistent with Scheme I. Comparison of runs 4 and 5 in Table II suggests that Co(TPP)·NO (IIa) is a better catalyst than py·Co(TPP)·NO_2 (II). A similar phenomenon was observed in the oxidation of alcohols catalyzed by a combination of Lewis acids with either II or IIa.[3] This was attributed to the interaction of Lewis acids with pyridine liberated from I or II after their reduction to the 5-coordinate nitrosyl complexes.[8] In the case of olefin oxidation, the pyridine released from I or II evidently

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(4) Maitlis, P. M. "The Organic Chemistry of Palladium", Academic Press: New York, 1971; Vol. I and II.

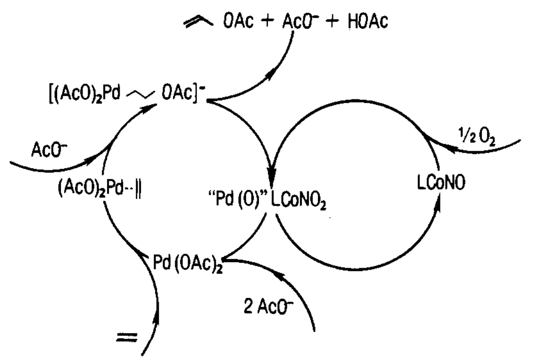
(5) Kharash, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

(6) Determined by GC analysis on a 1.8-m (6 ft) column containing 10% Carbowax supported on a 80/100 Supelcoport or a 2.4-m (8 ft) Porapak QS column in a Hewlett-Packard 5710A instrument equipped with a flame ionization detector. The yields are determined by computer integration, employing biphenyl as the internal standard.

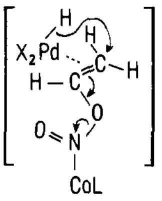
(7) Determined by IR spectroscopy after solvent evaporation from the reaction mixture aliquots and trituration with petroleum ether in an argon atmosphere.

(8) Five-coordinate cobalt–nitrosyl complexes display little affinity for base coordination. Compare also: Clarkson, S. G.; Basolo, F. *Inorg. Chem.* **1973**, *12*, 1528.

Scheme II



inhibits the ability of palladium(II) to coordinate olefins and to assist in the reoxidation of cobalt-nitrosyl complexes.[9] Acetaldehyde formation from intermediate V likely proceeds via β-hydride elimination followed by hydride shift and oxidation involving intermediate VI.



VI

Cobalt-Nitro Complexes as Palladium Oxidants. Cobalt-nitro complexes I and II are very weak nucleophiles. Therefore, the presence of almost any other competing nucleophile in the above system should result in Wacker-type chemistry. Thus, in acetic acid (Table I, run 7), vinyl acetate is the sole product when ethylene is oxidized by a mixture of cobalt-nitro complex and palladium(II) acetate in an *oxygen-free* atmosphere and *deoxygenated* acetic acid. Importantly, the yield of vinyl acetate is 100% based on the total of $Pd(OAc)_2$ and I. Again, the nitro complex I is cleanly reduced to the corresponding nitrosyl complex Ia. Furthermore, passing oxygen and ethylene into an acetic acid solution of $Pd(OAc)_2$ with either I or II results in the catalytic formation of vinyl acetate. In the catalytic oxidation, the rate of vinyl acetate formation is linear with time, and no metal deposition is apparent. In the absence of I or II, the oxidation is not catalytic, and palladium metal precipitates. These observations clearly underscore the ability of cobalt-nitro complexes to function as efficient reoxidants of palladium(0).[10] Thus, in the presence of nucleophiles, the cobalt-nitro complexes play a similar role to copper(II) in the classical Wacker process (Scheme II).

Conclusion. We have demonstrated a novel model of catalytic olefin oxidation by molecular oxygen. It involves oxygen transfer from the nitro ligand of cobalt-nitro complexes to palladium(II)-bound olefins followed by reoxidation of the reduced nitrosyl ligand by molecular oxygen. The palladium *remains* in the divalent state throughout the catalytic cycle and serves exclusively as a cocatalyst. Our future effort will be directed toward modifying the system to produce glycol derivatives or possibly epoxides.

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[9] The cobalt-nitrosyl complexes cannot be reoxidized in the absence of a base or palladium(II). The role of Pd(II) is not fully understood at this time, but it may be analogous to the role of Lewis acids; see ref 3.

[10] No formation of ethylene glycol mono- or diacetates is observed. These products might arise from oxidation of the Pd-C bond in the $[X_2PdCH_2CH_2OAc]^-$ intermediate by cobalt-nitro complexes in analogy to the behavior of $LiNO_3$; see: Tarura, M.; Yasui, T. *Kogyo Kagaku Zasshi* **1969**, *72*, 575, 578, 581, 585.

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A Direct NMR Method for the Determination of Correlation Times in Enzyme Complexes Involving Monovalent Cations and Paramagnetic Centers

Sir:

A persistent problem associated with using NMR methods to determine internuclear distances between paramagnetic centers and ligands bound to a macromolecule is the determination of the correlation time, τ_c, for the electron-nuclear interaction.[1] Practice has shown that the dipolar electron-nuclear interaction dominates the relaxation processes for several paramagnetic species and that relaxation can be described by the Solomon-Bloembergen equation.[2] The simplified form of this equation applicable to longitudinal relaxation data obtained with paramagnetic centers and $\tau_c \geq 10^{-10}$ s is given by eq 1, where r is the electron-nuclear

$$r = C\left[T_{1M}\cdot\frac{3\tau_c}{1+\omega_I^{2}\tau_c^{2}}\right]^{1/6} \qquad (1)$$

distance, C is a collection of constants whose value depends on the spin of the paramagnetic center and the gyromagnetic ratio of the nucleus, T_{1M} is the spin-lattice relaxation time attributable to the influence of the paramagnetic species, and ω_I is the nuclear Larmor precession frequency. This treatment also assumes fast exchange conditions and therefore that $1/T_{1p} = 1/T_{1M}$, where $1/T_{1p}$ is the observed relaxation rate corrected for diamagnetic effects.

Several methods have been described to estimate a value of τ_c for use in calculating distances: (1) measurement of T_1 and T_2 values for the nuclei, (2) a frequency dependence of T_1 of the nuclei, (3) a frequency dependence of the relaxation rates of solvent water in the system, and (4) measurement of the line width of the EPR spectrum of the paramagnetic species. Of these, the measurement of the frequency dependence of T_1 of the nuclei under observation gives the best results but of course requires that data be obtained by using two spectrometers or a single spectrometer with a variable field electromagnet. Also, for some ions, e.g., Mn^{2+} and Cu^{2+}, the relevant correlation time for the dipolar relaxation is the electron spin relaxation time which itself can be magnetic field dependent, further complicating the data analysis.

With these considerations in mind, we pursued NMR studies of several alkali metal ions in an attempt to measure distances between the monovalent-divalent cation sites of pyruvate kinase. Recently, two laboratories have reported the internuclear distance between Mn^{2+} and $^7Li^+$ bound to pyruvate kinase from rabbit muscle.[3] Ash et al.[3b] obtained a distance of 4.7 Å while Hutton et al.[3a] obtained a distance of 5.8 Å. The major reason for the difference in the measured distance is in the choice of the correlation time for the dipolar interaction. On the basis of water proton relaxation rate studies, Ash et al.[3b] and Hutton et al.[3a] used a τ_c value of 1.7 and 9.4 ns, respectively.

It occurred to us that an unambiguous determination of the correlation time could be made by performing identical experiments with $^6Li^+$ and $^7Li^+$ at the same magnetic field strength, thus obviating many of the problems discussed above.[4] From the ratio of the observed T_{1p} (T_{1M}) values for $^6Li^+$ and $^7Li^+$, a unique value of τ_c is obtained because in eq 1 C and ω_I are known values for the two isotopes of lithium, and the distance r must be the same

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[1] Dwek, R. A. "Nuclear Magnetic Resonance in Biochemistry", Clarendon Press: Oxford, 1973; Chapter 10.

[2] Solomon, I.; Bloembergen, N. *J. Chem. Phys.* **1956**, *25*, 261.

[3] (a) Hutton, W. C.; Stephens, E. M.; Grisham, C. M. *Arch. Biochem. Biophys.* **1977**, *184*, 166. (b) Ash, D. E.; Kayne, F. J.; Reed, G. H. *Ibid.* **1978**, *190*, 571.

[4] Reuben, J. *J. Chem. Phys.* **1975**, *63*, 5063. Reuben measured ^1H and ^2H relaxation rates at one magnetic field strength in order to determine if $\tau_M > T_{1M}$ in aqueous solutions containing Gd^{3+}. In principle, our approach is analogous to this, but we apply the multiple isotope method to determine the correlation time for the dipolar relaxation induced by a paramagnetic species on monovalent cations in macromolecular complexes. The method we describe is valid for any two isotopes that have the same chemical properties in the system under analysis, e.g., both are cations or both are organic derivatives with ^{14}N or ^{15}N isotopes, and so forth. This method demands that $\tau_M > T_{1M}$.