Table I, Spectra of Mono-COT Thorium Compounds

no.	compound	spectrum
		^{1}H NMR, δ (ppm from Me_4Si)
1a	$C_8H_8ThCl_2$	6.79 (s, ring)[a,b] 6.6 (s, ring)[c]
1b	n-$C_4H_9C_8H_7ThCl_2$	6.6 (ring)[c] 3.1, 1.0 (Bu)
1c	1,3,4,7-$Me_4C_8H_4ThCl_2$	6.5 (ring)[c] 3.1 (Me)
2a	$C_8H_8Th(BH_4)_2$	6.69 (s, 8 H, ring), 3.11 (q, J = 85 Hz, 8 H, BH_4), 3.34, 0.90 (br, 8 H, THF)[a]
		^{13}C NMR, δ (ppm from Me_4Si)
1b		116.5, 104.1, 103.1, 102.7, 101.2 (ring), 49.5, 38.6, 22.8, 14.5 (Bu)[c]
		IR (Nujol), cm^{-1}
2a		2482 (s) (B–H, terminal), 2282 (w), 2220 (s), (B–H, bridging), 2150 (m), 1180 (s), 1163 (s), 722 (sh), 714 (s) (COT)

[a] In C_6D_6. [b] Also showed resonances for THF, 3.69 (t), 13.6 (m); areas for the three resonances are 1:1:1, consistent with $C_8H_8ThCl_2 \cdot 2THF$. [c] In THF-d_8.

we hoped that replacement of chloride by borohydride would result in more volatile complexes. Also of interest is the nature of the bonding of the borohydride groups to the metal center; both tridentate and bidentate bonding to the BH_4 groups are known for actinide compounds.[8] The preparation of $C_8H_8Th(BH_4)_2$ (**2a**) and n-$C_4H_9C_8H_7Th(BH_4)_2$ (**2b**) has been achieved by several routes. Refluxing an equimolar mixture of $Th(BH_4)_4(THF)_2$[9] and di-n-butylthorocene[3] in THF gave **2b** in 67% yield. Because of the low solubility of thorocene, **2a** is more easily prepared by the reaction of equimolar amounts of $Th(BH_4)_4(THF)_2$ and K_2COT in THF at room temperature. We also prepared **2a** by the sequence

$$ThCl_4 + 2LiBH_4 \xrightarrow{THF} \text{“}ThCl_2(BH_4)_2\text{”} \xrightarrow[THF]{K_2COT} \underset{\mathbf{2a}}{C_8H_8Th(BH_4)_2}$$

This route is made more complicated, however, by the necessity to remove the LiCl also formed.

2a and **2b** are white microcrystalline products soluble in THF and benzene but not volatile. Satisfactory combustion analyses were not obtained,[10] but the compounds were well characterized by NMR and IR spectra (Table I). The ^{1}H NMR spectrum of **2a** in C_6D_6 shows two molecules of coordinated THF in addition to the COT and two equivalent BH_4 groups. The quartet from the borohydride protons is similar to that in $(C_5H_5)_3ThBH_4$[8a] and indicates fluxional behavior among these protons. At −80 °C the quartet collapses to a broad singlet at δ 3.0 and, as noted by Marks and Shimp,[11] probably indicates a temperature-dependent loss of B–H coupling rather than a slowing of the fluxional process. The IR spectrum is in accord with tridentate binding to borohydride. The 2500-2100-cm^{-1} region is similar to that for $Th[N(SiMe_3)_2]_3BH_4$ for which tridentate geometry has been established by crystal structure determination.[12] The strong band at ~715 cm^{-1} (15 cm^{-1} higher than a band in thorocene) appears to be characteristic of the mono-ring or "half-sandwich" structure.

All of these compounds are air and moisture sensitive. The further chemistry of these compounds is being studied.

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(10) Combustion analyses varied with handling of the sample in a manner indicative of weakly bound and nonstoichiometric THF (see note 4). A typical result for a sample kept at 10^{-6} Torr overnight follows. Calcd for $C_8H_8Th(BH_4)_2 \cdot 0.8C_4H_8O$: C, 31.76; H, 5.33. Found: C, 31.80; H, 5.34. A sample without such prolonged pumping showed more THF. A different sample was used for NMR measurement which showed still greater THF (2 equiv). Qualitative analysis indicated thorium.

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Carole LeVanda,[13] Jeffrey P. Solar, Andrew Streitwieser, Jr.*
Department of Chemistry, University of California
and Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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Olefin Epoxidation by an Intermediate Formed in the Metal Ion Catalyzed Oxygenation of Azibenzil

Sir:

Many monooxygenase-catalyzed reactions involve a species which transfers an oxygen atom to the substrate. One model for this species is the "oxenoid" intermediate.[1] Much attention has been devoted to the structure and reactivity of carbonyl oxides as model oxenoids, which are proposed to be formed as intermediates in ozonation of alkenes,[3] alkynes,[4] and ketenes.[5] Intermediates in the photooxygenation of diazo compounds[6] and singlet oxygen oxygenation of diazo compounds and ylides[7] are probably similar in structure and can also transfer oxygen to alkanes,[8] alkenes,[9] sulfides,[10] and aromatic substrates.[11] We now report that azibenzil reacts readily with oxygen in the presence of metal ion catalysts to give an intermediate which can transfer an oxygen atom to olefins to give epoxides under very mild conditions.

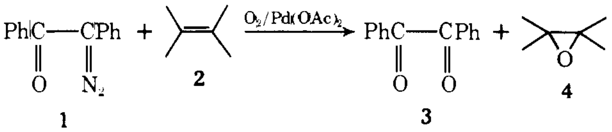

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Table I. Olefin Epoxidation by an Intermediate Formed in the Pd(OAc)$_2$-Catalyzed Oxygenation of Azibenzil[a]

no.	olefin **2**	rel reactivity[b]	product yield, %[c]		
			PhCOCOPh (**3**)	epoxide **4**	other
	none		85		
a	1,2-dimethyl cyclohexene	1.0	87	71	
b	1-methylcyclohexene	0.2	75	59	
c	cyclohexene	0.02	85	24	
d	2,3-dimethyl-2-butene	2.0	90	87	
e	*cis*-3-hexene	0.011	85	10 (*trans*) 3 (*cis*)	
f	*trans*-3-hexene	0.011	85	11 (*trans*) <1 (*cis*)	
g	α-methylstyrene		74	43	22 (PhCOMe)
h	*cis*-β-methylstyrene		82	43 (*trans*) 3 (*cis*)	40 (PhCHO)
i	*trans*-β-methylstyrene		91	40 (*trans*)	41 (PhCHO)

[a] Reaction was performed at room temperature in CH$_2$Cl$_2$ (15 mL) containing azibenzil (0.1 mmol), Pd(OAc)$_2$ (5×10^{-3} mmol) and olefin (2 mmol). Oxygen was bubbled through the solution during the reaction. [b] By competition experiments. [c] Yields were determined by GLC (internal standard technique) based on azibenzil used. Benzophenone formation was <3% in all cases reported in this table.

A solution of azibenzil **1** (0.1 mmol) and olefin **2** (2 mmol) in CH$_2$Cl$_2$ (15 mL) was stirred for 8 h at room temperature in the presence of Pd(OAc)$_2$ (5×10^{-3} mmol).[12] Oxygen was bubbled through the solution during the reaction. The results are shown in Table I.

In the case of aliphatic and alicyclic olefins, benzil (**3**) and epoxides (**4**) were the major oxidation products. No products from either singlet oxygen or radical autoxidation were formed.[13] When aromatic olefins were used, epoxide formation was accompanied by oxidative cleavage of the double bond. In the absence of the olefin, benzil was a main product; no benzophenone was detected.

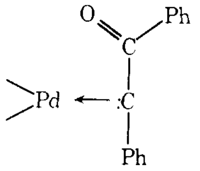
Reaction in benzene gave similar results. However, use of acetonitrile as solvent led to a drastic reduction in yields of both **3** and **4**, and benzophenone was the main product. When the reaction was carried out at 80 °C in benzene without catalyst, **3** and **4** were minor products (<1%) and benzophenone was the major product. Benzophenone probably arises from the oxidation of diphenylketene[14] obtained via Wolff rearrangement of the ketocarbene.[15]

When trans olefins (**2f, 2i**) were epoxidized, only trans epoxides were formed; however, cis olefins (**2e, 2h**) gave both cis and trans epoxides, with the trans product predominating. The lack of stereospecificity of the reaction resembles the results in α-diketone-sensitized epoxidation,[16] indicating a stepwise mechanism with an intermediate which can rotate.

The relative reactivities of the olefins were measured by competition experiments (Table I). The observed alkyl substituent effects show that the intermediate is mildly electrophilic and does not have kinetic cis-trans selectivity.

There have been several reports on olefin oxidations catalyzed by oxygen-carrying group 8 metal complexes.[17] However, the catalyst and oxygen alone did not bring about any olefin oxidation in our system, indicating that **1** is necessary for epoxidation.

To obtain information about the role of the catalysts in decomposition of **1** and in the suppression of Wolff rearrangement, we examined the reaction using dichlorobis(benzonitrile)palladium, which reacts with **1** under milder conditions than other Pd(II) catalysts. An equimolar solution of **1** and (PhCN)$_2$PdCl$_2$ in CH$_2$Cl$_2$ was warmed under N$_2$ from −78 °C to room temperature. When the temperature reached 10–20 °C, N$_2$ evolution was observed and brown crystals of a complex **5** (>90%, dec pt 155 °C)[18] were obtained. Reaction of **5** with O$_2$ in the presence of excess **2d** under the reaction conditions resulted in the recovery of the starting materials. However, when **1** was mixed with an equal amount of (PhCN)$_2$PdCl$_2$ and excess **2d** at −78 °C and then slowly warmed under a stream of O$_2$, olefin epoxidation was observed along with the formation of benzil at the same temperature at which N$_2$ evolution occurred.[19] The results indicate that the catalyst accelerates the decomposition of azibenzil to form an intermediate, probably ketocarbene-metal complex **6**,[20] which subsequently reacts with O$_2$ to form the second intermediate which transfers an oxygen atom to olefins. In the absence of O$_2$, intermediate **6** rearranges to give **5**, which is not an oxygenation catalyst. The formation of **3** in preference to cyclopropanation[21] indicates that intermediate **6** is more reactive toward oxygen than toward olefins.



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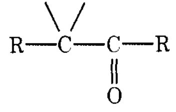
Keay and Hamilton have reported that ozonation of alkynes gives at least three apparently different epoxidizing species, and they have proposed structure **8** for the "intermediate-temperature" species, which reacts with cis olefins more than an order of magnitude more rapidly than with trans olefins to give trans epoxides in a nonstereospecific manner.[4b] The lack of kinetic cis-trans selectivity of the reaction in our system (relative reactivity: *cis*-3-hexene:*trans*-3-hexene ≈ 1:1) suggests that the intermediate has slightly different characteristics from that in alkyne ozonation.

Michejda and Campbell have reported that epoxidation is observed when olefins are treated with tetramethyl-2-tetrazene, ZnCl$_2$, and O$_2$. A complex (**9**) has been proposed to be the oxygen-transferring intermediate.[24] A similar (although even-electron) intermediate **10** (or its alternatives **11** or **12**)



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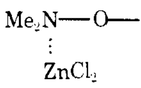

$$\underset{\textstyle\vdots\atop\textstyle \mathrm{ZnCl_2}}{\mathrm{Me_2N}}\text{—O—O}\cdot$$

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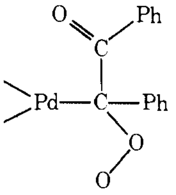

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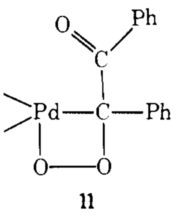

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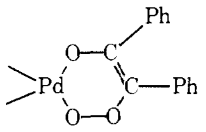

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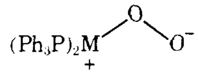

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would be a plausible oxygen transfer reagent in the present system.

Low-oxidation-state dioxygen complexes react with electron-deficient, but not electron-rich, olefins to give stable complexes. A nucleophilic zwitterion intermediate (**13**) analogous to the Criegee intermediate has been suggested.[17e] The oxidation of cyclohexene catalyzed by these metal complexes has been shown to give radical autoxidation products.[17b] The results presented here clearly indicate that the reactivity of our intermediate toward olefins is quite different from these complexes.

In summary, we have found a new oxygen-transfer agent which involves an intermediate metal oxygen-carbene complex and which epoxidizes olefins. Investigation of the mechanism and scope of the reaction is currently underway.

Acknowledgment. This work was supported by Public Health Service Grant No. GM 20080.

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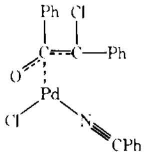

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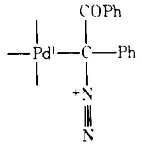
(19) The reaction was checked by GC and LC at −30, −10, 0, 10, and 20 °C after removal of O_2 by flushing with N_2. Below 10°, no epoxidation was observed.
(20) An alternative path in which N_2 evolution and O_2 attack occur simultaneously in intermediate **7** might be considered. However, **6** is a preferable formulation because the formation of benzophenone as an oxidation product would require the formation of a free ketocarbene which could be formed by a nucleophilic attack of acetonitrile on **6**, but not on **7**. This formulation is consistent with the effects of base on the reaction of $Cu(acac)_2$ with diazoacetophenone[22] and the instability of carbene complexes to nucleophiles.[23]



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Hong-Son Ryang, Christopher S. Foote*
Department of Chemistry, University of California
Los Angeles, California 90024
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Synthesis and Absolute Configuration of 4,5-Diazatwist-4-ene

Sir:

Relative to the work which has been expended on its isoelectronic counterparts (olefins and ketones), the azo group has been neglected. To the spectroscopist, the underlying reason probably resides in the fact that diimide, the parent azo compound, has only a transient existence,[1] unlike ethylene and formaldehyde. Nevertheless, the optical activities of a few trans azo alkanes[2] and several chiral pyrazolines[3,4] have been measured. In fact, the rotational strengths of the circular dichroic (CD) spectra of these compounds suggest the possible utilitarian role of the azo group as a probe of asymmetric environment within molecules. In view of these earlier findings and the considerable interest which twistene has commanded,[5] we have been prompted to prepare 4,5-diazatwist-4-ene (**1**) in optically active form with full knowledge of the absolute configuration. The molecular rigidity present in **1** presumably[6] fixes the -N=N- unit into an essentially planar cisoid geometry.

The pivotal substrate in this study is (−)-*endo*-bornyl-1,2,4-triazolinedione (**3***) which is readily synthesized in optically pure form from *d*-camphor.[7] The absolute configuration of this dienophile is, therefore, as drawn.[8] Addition of **3*** to cyclooctatetraene dibromide (**2**) afforded an adduct, which when directly debrominated[9] delivered **4***, mp 193–194 °C, $[\alpha]_D$ −6.6° (*c* 12.8, C_2H_5OH), in 92% overall yield.[10] The subsequent irradiation of **4*** in benzene-acetone solution (1:1) with a 450-W Hanovia lamp through a Vycor filter resulted in cyclization (84%) to **5***, mp 192.5–193 °C, $[\alpha]_D$ −4.34° (*c* 8.3, C_2H_5OH). By means of regiocontrolled hydrogenolysis,[11] this basketane derivative was quantitatively converted into a mixture of the diheterotwistane diastereomers **6*** and **7***, $[\alpha]_D$ −6.0° (*c* 7.5, C_2H_5OH). Repeated recrystallization of this product from an ethyl acetate-pentane solvent system afforded colorless crystals, mp 213–213.5 °C, whose rotation, $[\alpha]_D$ −53.9° (*c* 5.9, C_2H_5OH), did not change upon further processing. Hydrolysis-oxidation of this material by suitable modification of the conditions of Askani and Schwertfeger[12]

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