C7, O1, and O2.[9] While 5 contains an essentially planar Cu_2O_2 bridging framework, this is butterfly shaped in 4; the dihedral angle between planes formed by Cu1, O1, and O2 and by Cu2, O1, and O2 is 18.0°. Most other bond distances and angles are alike except for those affected by the presence of the one five-membered ring present in 4 (Cu1). One manifestation of the structural differences is the less efficient antiferromagnetic coupling between Cu(II) ions observed in the unsymmetrical complex 4 compared to symmetric complex 5; the room temperature magnetic moments are $1.5 \pm 0.1 \ \mu_B/Cu$ vs $0.8 \ \mu_B/Cu$, respectively.[21]

The present study shows that the relatively small modification in dinucleating ligand effected here causes a substantial change in reactivity pattern with dicopper(I) complex 1. We have attributed the selective and rapid hydroxylation of the arene moiety in 2 to the close and appropriate proximity of the reacting peroxo–dicopper species (with μ-η^2:η^2 structure[15]) with the XYL ligand.[2,10] Here, we qualitatively observe that the initial oxygenation of 1 is still very rapid, but that the ensuing hydroxylation is considerably slowed.[13] We suggest that the latter is due to (a) altered electronic influences on the arene ring or attacking peroxo species and/or (b) constraints of the modified UN ligand, disrupting an orientation of the Cu-(O_2)–Cu and arene substrate moieties which is preferable for rapid reaction. Further studies will address these and other issues utilizing unsymmetrical dinucleating ligands.

Supplementary Material Available: Listings of crystal data and experimental conditions, atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for 4 (7 pages); listing of observed and calculated structure factors for 4 (12 pages). Ordering information is given on any current masthead page.

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Low-Temperature, Palladium(II)-Catalyzed, Solution-Phase Oxidation of Methane to a Methanol Derivative

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Methane is the most abundant and the least reactive member of the hydrocarbon family. Thus, the selective oxidation (preferably, catalytic) of methane under mild conditions is one of the most challenging chemical problems, in addition to being of great practical importance. The number of reported methods for the selective, low-temperature ($\sim$100 °C or below) oxidation of methane is very limited indeed. For example, the radical-initiated chlorination of methane is very nonselective and invariably leads to multiple chlorinations[1] (chlorination, however, is more specific in the presence of superacids[2]). Among transition-metal-*mediated* procedures, the only one that gives good yields involves $PtCl_4^{2-}$–catalyzed oxidation of methane by $PtCl_6^{2-}$ in water at 120 °C, which leads to the formation of equal amounts of methanol and methyl chloride.[3]

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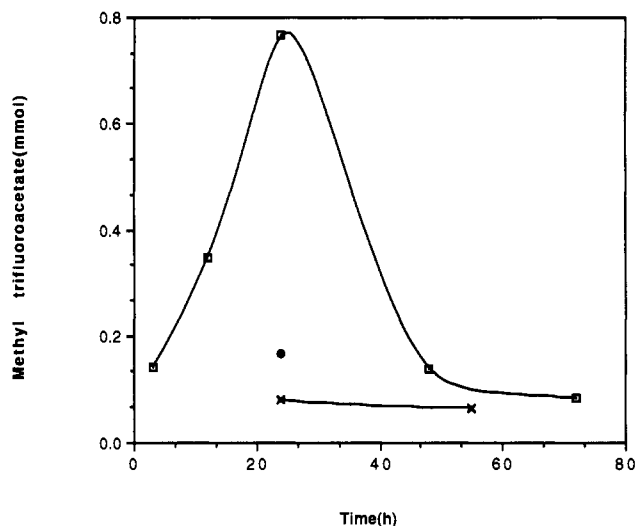
Figure 1. Yield of methyl trifluoroacetate versus time. Conditions: 90 °C, CH_4 (900 psi), $(CF_3CO)_2O$, 1.8 mL; (×) 30% H_2O_2 (2 mmol); (□) 30% H_2O_2 (2 mmol) + $Pd(O_2CC_2H_5)_2$ (0.15 mmol); (●) 30% H_2O_2 (2 mmol) + Pd black (0.15 mmol).

We have now discovered that peroxytrifluoroacetic acid (generated from hydrogen peroxide and trifluoroacetic anhydride) oxidizes methane specifically to methyl trifluoroacetate, CF_3C-O_2CH_3. Furthermore, this reaction is catalyzed by the Pd(II) ion. Our results are illustrated in Figure 1. Since the product, $CF_3CO_2CH_3$, can be hydrolyzed to methanol, the overall reaction may be written as shown in eq 1. The purpose of having an excess

$$CH_4 + H_2O_2 \xrightarrow[90 \ °C]{Pd(II), \ (CF_3CO)_2O} CH_3OH + H_2O \qquad (1)$$
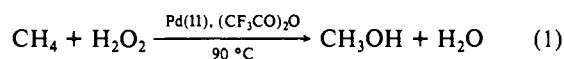
of trifluoroacetic anhydride is to remove the water generated, thereby preventing the hydrolysis of the ester to the more easily oxidized methanol. Ready further oxidation (eventually to CO_2 and H_2O) of the primary products is a persistent problem in the area of selective oxidation of alkanes. As is evident from Figure 1, our strategy works to a certain extent; however, at long reaction times, further oxidation of $CF_3CO_2CH_3$ does occur. Significantly, this latter oxidation step is also catalyzed by Pd(II) since CF_3C-O_2CH_3 was found to be stable in the reaction mixture in the absence of the metal.

The following observations seem to indicate an electrophilic, rather than radical, mechanism for the oxidation of methane. The oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane to the corresponding tertiary alcohols by peroxytrifluoroacetic acid was previously shown to proceed by complete retention of configuration.[4] The addition of the Pd(II) ion to the system does not appear to alter the mechanism since, when *p*-xylene was used as the substrate, the ratio of esters derived from the attack on the ring versus the benzylic position was >100:1. Therefore, a radical pathway is not involved since the weak benzylic C–H bonds were not broken. One mechanism that is consistent with the above observations involves attack by an incipient OH^+ and proceeds through the following transition state.[5] Under this scenario, the
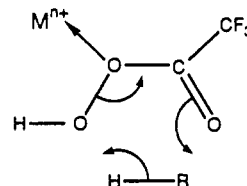

Pd(II) ion promotes the reaction by coordination to the α-oxygen

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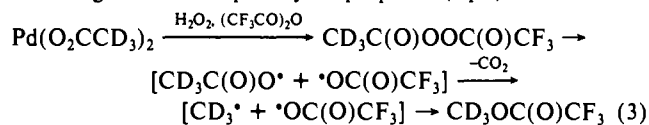(5) Deno, N. C.; Jedziniak, E. J.; Messer, L. A.; Meyer, M. D.; Stroud, S. G.; Tomezsko, E. S. *Tetrahedron* **1977**, *33*, 2503.

atom thereby further polarizing the O–O bond.[6]   Other metal ions should also have a similar effect. However, the substitution of $Pd(O_2CC_2H_5)_2$ by either $Pb(O_2CCH_3)_4$, $Fe(O_2CCH_3)_2$, or $Co(O_2CCF_3)_2$[7] resulted in a yield of $CF_3CO_2CH_3$ that was either similar to or only marginally higher than that observed with peroxytrifluoroacetic acid alone. An alternative role of the Pd(II) ion can be envisaged based on our previous observation[8] that the Pd(II) ion will oxidize methane under stoichiometric conditions through a step involving an electrophilic attack on a methane C–H bond (eq 2).   A parallel catalytic oxidation pathway may,

$$CH_4 + Pd(O_2CR)_2 \xrightarrow[90\ °C]{CF_3CO_2H} CF_3CO_2CH_3 + Pd(0) + 2RCO_2H \quad (2)$$
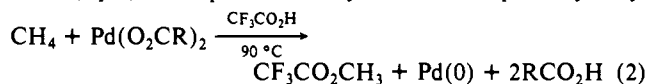
therefore, ensue upon the addition of the Pd(II) ion to the system. The catalytic cycle would combine the reaction shown in eq 2 with a step involving the reoxidation of Pd(0) to Pd(II) by peroxytrifluoroacetic acid. In principle, it should be possible to initiate the catalytic cycle by starting with Pd(0). The addition of "palladium black" to peroxytrifluoroacetic acid did result in an enhanced yield of $CF_3CO_2CH_3$; nevertheless, the effect was much less than that observed with $Pd(O_2CC_2H_5)_2$ (Figure 1). This observation does not necessarily rule out the above catalytic cycle since, in several catalytic oxidations involving the Pd(II)/(0)/(II) cycle, it has been observed that once Pd(0) is allowed to aggregate, it cannot be easily reoxidized to Pd(II).[9]

The final point concerns the use of $Pd(O_2CC_2H_5)_2$ for methane oxidation. $Pd(O_2CCH_3)_2$ was also effective in promoting oxidation of methane by peroxytrifluoroacetic acid. However, studies involving $Pd(O_2CCD_3)_2$ indicated that a fraction (15–20%) of the acetate ligand was converted to $CF_3CO_2CD_3$ in the presence of peroxytrifluoroacetic acid. On the basis of previous reports,[10] the following series of steps may be proposed (eq 3).

$$Pd(O_2CCD_3)_2 \xrightarrow{H_2O_2,\ (CF_3CO)_2O} CD_3C(O)OOC(O)CF_3 \rightarrow$$

$$[CD_3C(O)O^\bullet + {}^\bullet OC(O)CF_3] \xrightarrow{-CO_2}$$

$$[CD_3{}^\bullet + {}^\bullet OC(O)CF_3] \rightarrow CD_3OC(O)CF_3 \quad (3)$$

Therefore, in order to remove all ambiguity concerning the source of the methyl group in CF_3CO_2Me, $Pd(O_2CC_2H_5)_2$ was used as the source for the Pd(II) ion. A further advantage of using the propionate salt is that, due to its greater stability, any ethyl radical generated is unlikely to abstract a hydrogen atom from methane to generate the corresponding methyl radical. No $CF_3CO_2CF_3$ was observed when $Pd(O_2CCF_3)_2$ was treated with peroxytrifluoroacetic acid presumably due to the low stability of the trifluoromethyl radical. However, this latter Pd(II) species was not used for methane oxidation due to its insolubility in the reaction medium.

In conclusion, we have demonstrated that it is possible to achieve the selective, catalytic oxidation of methane through an electrophilic pathway under mild conditions.[11]   It is worthwhile noting that the biological oxidation of methane[12] also involves a metal-catalyzed reaction of methane with a hydrogen peroxide equivalent (eq 4).   In analogy with the biological oxidation of higher hydrocarbons, it has been proposed that the mechanism

$$O_2 + 2H^+ + 2e^- \rightarrow [H_2O_2] \xrightarrow{CH_4} CH_3OH + H_2O \quad (4)$$
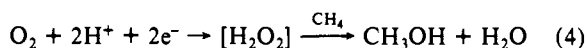
of methane oxidation involves the intermediacy of a methyl radical.[13]   However, the methyl radical is a particularly high energy species, and such a mechanism has never been demonstrated in a nonbiological system, except under photolytic conditions[1] or at very high temperatures.[14]   In view of our results, we believe that an alternative electrophilic mechanism should be considered for biological methane oxidations especially since high-valent, electrophilic metal species are believed to be involved.[8a]

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A Pd-Catalyzed Zipper Reaction

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Recently, we have focused on developing reactions wherein the product is the simple sum of the reactants.[1]   When applied intramolecularly, such reactions become cycloisomerizations.[2–4]   Considering the importance of cationic initiated polyolefin cyclizations,[5] the prospect of polyolefin cyclizations catalyzed by transition metals becomes extremely attractive because of the control that transition-metal templates may exercise. In this paper, we report the realization of a polyolefin polycycloisomerization.[6,7]

Our investigation began with the cis-1,4-disubstituted cyclopentene 1[8] because of its ready accessibility from the monoepoxide of cyclopentadiene using Pd(0) chemistry. Warming a 0.4 M benzene solution of dienyne 1 containing 2.5 mol % (dba)$_3$Pd$_2$·CHCl$_3$, 10 mol % triphenylphosphine, and 10 mol % acetic acid

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