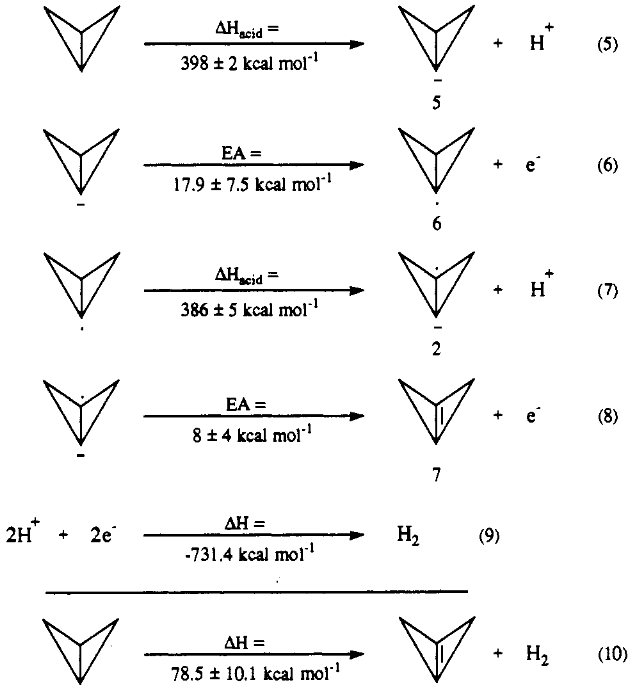
surements of the acidity of bicyclo[1.1.0]butane and the electron affinity of its corresponding radical (eqs 5 and 6)[13] can be combined with our current determination of the proton and electron affinity of **2** and **7** (eqs 7 and 8)[14] in a thermodynamic cycle (eqs 5–10) to afford the heat of hydrogenation for bicyclo[1.1.0]-but-1(3)-ene (**7**). The experimentally derived value is 78.5 ± 10.1 kcal mol^{-1} and is in excellent agreement with recent computations by Hrovat and Borden, Schaefer et al., and Wiberg, Bonneville, and Dempsey (82.3 (TCSCF 6-31G*), 76.1 (DZP 2R CIDVD//6-31G* 2R CISD), and 91 kcal mol^{-1} (6-31G*), respectively).[8b,15] In addition, the heats of formation of **5**, **6**, **2**, and **7** (84 ± 2, 102 ± 8, 122 ± 9, and 130 ± 10 kcal mol^{-1}, respectively) have been derived.



Examination of a variety of additional compounds, including several strained ring systems, reveals that the formation of (M – 2) ions is a fairly general process. The structure and reactivity of these radical anions are currently being explored and should provide a wealth of thermodynamic information on a variety of reactive intermediates.

Acknowledgment. We thank Gregg Dahlke for his assistance in the initial experiments and for carrying out several of the molecular orbital calculations. Support from the Minnesota Supercomputer Institute, University of Minnesota McKnight Land Grant Professorship program, and the National Science Foundation (CHE-8907198) is gratefully acknowledged.

Supplementary Material Available: Electron affinities and LUMO energies for all structures and a plot of their correlation (2 pages). Ordering information is given on any current masthead page.

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(14) Proton transfer is observed between **2** and *t*-BuOH, EtOH, and MeOH but not with H_2O (ΔH_{acid} = 375, 377, 381, and 391 kcal mol^{-1}, respectively). The proton affinity is therefore assigned a value of 386 ± 5 kcal mol^{-1}. Electron transfer occurs between **2** and SO_2, biacetyl, CS_2, cyclooctatetraene, and O_2 (EA = 25.6, 16.2, 13.8, 13.1, and 10.4 kcal mol^{-1}, respectively), and therefore 10.4 kcal mol^{-1} can be taken as an upper limit for the electron affinity of **7**. A reasonable lower limit is 5 kcal mol^{-1} since ions with electron affinities below this value rapidly undergo electron detachment and are difficult to observe, at room temperature, in a flowing afterglow device (He buffer gas). Consequently, the electron affinity is taken to be 8 ± 4 kcal mol^{-1}. References for the EAs are as follows. SO_2: (a) Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740. (b) Nimlos, M. R.; Ellison, G. B. *J. Phys. Chem.* **1986**, *90*, 2574. Biacetyl: (c) Grimsrud, E. P.; Caldwell, G.; Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 4627. CS_2: (d) Compton, R. N.; Reinhardt, P. W.: Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 45. Cyclooctatetraene: (e) Wentworth, W. E.: Ristau, W. *J. Phys. Chem.* **1969**, *73*, 2126. O_2: (f) Travers, M. J.; Cowles, D. C.; Ellison, G. B. *Chem. Phys. Lett.* **1989**, *164*, 449.

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Unsymmetrical Dicopper Complexes. Direct Observation of Reversible O_2 Binding in a Copper Monooxygenase Model System

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In modeling metalloenzyme Cu^I/O_2 interactions, the design and investigation of species containing unsymmetrically disposed dicopper ion centers is of interest, since there is good evidence for the inequivalence of copper sites in some proteins.[2,3] Here, we report the purposeful design, synthesis, and reactivity of a dinuclear complex $[Cu_2(UN)]^{2+}$ (**1**), containing unsymmetrically coordinated copper(I) ions.[8] In a transformation closely modeling that of copper monooxygenases,[9-11] **1** reacts with O_2 reversibly to give a stabilized and directly observable $\{Cu_2–O_2\}^{2+}$ species $[Cu_2(UN)(O_2)]^{2+}$ (**3**); upon warming, **3** further reacts to give hydroxylated complex $[Cu^{II}_2(UN\text{-}O\text{-})(OH)]^{2+}$ (**4**). This contrasts with the reactivity of the symmetric parent compound $[Cu^I_2(XYL)]^{2+}$ (**2**, derived from *m*-xylene diamine), where a reversibly formed $Cu_2–O_2$ intermediate was inferred only from a kinetic analysis.[10,11] Thus, within a single reaction sequence **1** → **4**, the elements of chemically reversible O_2 binding, spectroscopic identification of the $\{Cu_2–O_2\}^{2+}$ species, and O_2 activation are present (Scheme I).

Unsymmetrical compound **1**[12] displays an essentially featureless

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(1) (a) Johns Hopkins University. (b) SUNY Albany. Current address: Department of Chemistry, Syracuse University, Syracuse, NY 13244.

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(11) A kinetic study reveals that **2** reacts reversibly with O_2 giving a $\{Cu_2–O_2\}$ intermediate; in a second intramolecular step, hydroxylation occurs. Cruse, R. W.; Kaderli, S.; Karlin, K. D.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 6882–6883.

(12) $[Cu_2(UN)]^{2+}$ (**1**) was generated by addition of 2 equiv of $[Cu^I(CH_3CN)_4](PF_6)$ with the UN[13] in CH_2Cl_2 (Ar). The ^1H NMR spectra of both the UN free ligand and **1** reflect the difference in chemical environment of the two ligand arms.[13] Anal. for $[Cu_2^I(UN)(PF_6)_2$ [**1-(PF_6)$_2$**]. Calcd for $C_{35}H_{38}Cu_2F_{12}N_6P_2$: C, 43.79; H, 3.96; N, 8.74. Found: C, 44.28; H, 4.25; N, 8.74. ^1H NMR (300 MHz) (CD_3NO_2): δ 8.70 (d, 2 H), 8.45 (d, 2 H), 8.0 (m, 2 H), 7.85 (m, 2 H), 7.52 (d, 4 H), 7.40 (m, br, 4 H), 7.20 (m, 2 H), 6.92 (d, 1 H), 6.76 (s, 1 H), 3.6–3.8 (br, 6 H), 3.0–3.2 (br, 12 H).

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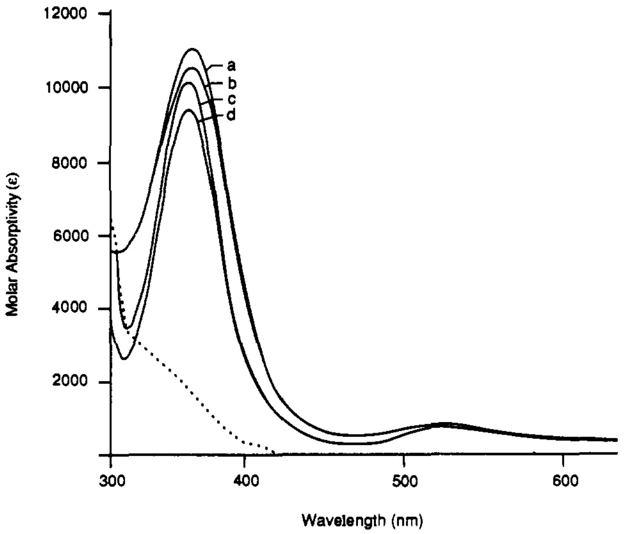
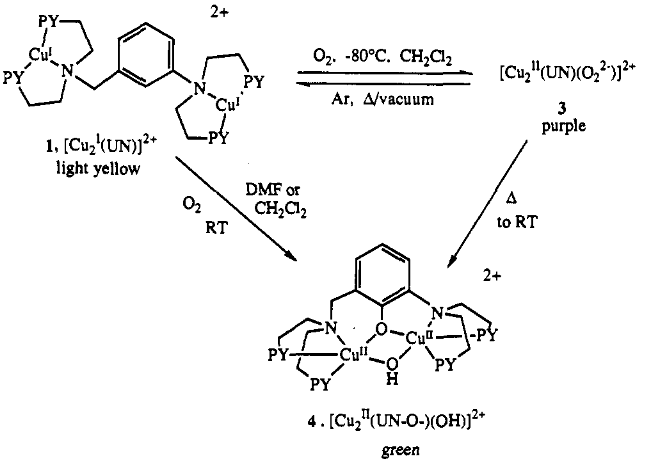


Figure 1. UV-vis spectra demonstrating the reversible O_2-binding behavior of $[Cu^I_2(UN)]^{2+}$ (**1**) in CH_2Cl_2. Deoxy complex **1** (---) (shoulder at 410 nm is an artifact) reacts with O_2 at −80 °C to give $[Cu_2(UN)(O_2)]^{2+}$ (**3**) (spectrum a). Application of a static vacuum during brief warming to 100 °C removes the bound O_2, regenerating **1** with its deoxy spectrum. Chilling (−80 °C) reoxygenation again produces **3** (spectrum b). Two additional deoxy/oxy cycles are shown.

Scheme I



UV-vis spectrum (Figure 1), but upon reaction with O_2 at −80 °C ($Cu:O_2 = 2:1$, manometry), a purple-colored species (**3**) is formed [$\lambda_{max} = 360$ nm ($\epsilon = 11\,000$ M^{-1} cm^{-1}), 520 nm ($\epsilon = 1000$ M^{-1} cm^{-1}), 600 nm (sh)]. The UV-vis pattern and the stoichiometry of reaction with O_2 suggest that $[Cu_2(UN)(O_2)]^{2+}$ (**3**) is a peroxo-dicopper(II) complex, having a μ-η^2:η^2 bridging structure similar to that proposed for closely related complexes $[Cu_2(Nn)(O_2)]^{2+}$ (**6**).[14,15]

Whereas the reaction of **2** with O_2 is rapid and irreversible even at −80 °C, dioxygen binding to **1** is reversible. Solutions of **1** can be repeatedly oxygenated and deoxygenated, since the application of a vacuum while $[Cu_2(UN)(O_2)]^{2+}$ (**3**) is being briefly heated causes decoloration and reversion to $[Cu_2(UN)]^{2+}$ (**1**). Four oxygenation/deoxygenation cycles can be carried out without severe decomposition (~20%) (Figure 1).

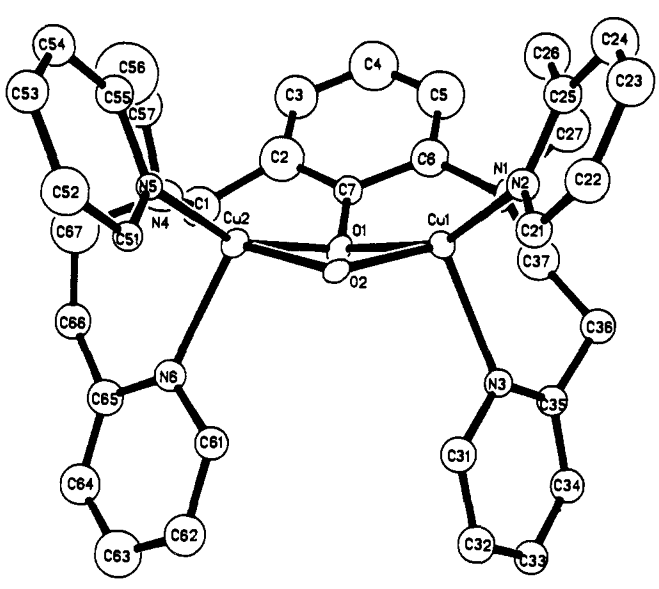


Figure 2. ORTEP diagram of the cationic parrt of complex $[Cu^{II}_2(UN\text{-}O\text{-})(OH)](PF_6)_2$ [**4-(PF_6)$_2$**] showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg) are as follows: Cu---Cu, 3.037 (5); Cu1–O1, 2.015 (18); Cu1–O2, 1.934 (18); Cu2–O1, 2.015 (21); Cu2–O2, 1.929 (17); Cu1–N1, 2.053 (28); Cu1–N2, 1.994 (18); Cu1–N3, 2.220 (17); Cu2–N4, 2.024 (31); Cu2–N5, 2.039 (16); Cu2–N6, 2.198 (19); O1–Cu1–O2, 77.5 (8); O1–Cu2–O2, 77.6 (7); O1–Cu1–N1, 82.7 (10); O1–Cu1–N2, 153.9 (8); O1–Cu1–N3, 102.8 (7); O1–Cu2–N4, 90.3 (10); O1–Cu2–N5, 155.4 (7); O1–Cu2–N6, 105.6 (8); O2–Cu1–N1, 156.9 (9); O2–Cu1–N2, 95.1 (8); O2–Cu1–N3, 98.1 (7); O2–Cu2–N4, 164.1 (10); O2–Cu2–N5, 93.3 (7); O2–Cu2–N6, 100.4 (8); N1–Cu1–N2, 97.5 (10); N1–Cu1–N3, 97.8 (9); N2–Cu1–N3, 103.0 (7); N4–Cu2–N5, 93.7 (10); N4–Cu2–N6, 92.6 (11); N5–Cu2–N6, 98.5 (7); Cu1–O1–Cu2, 97.8 (9); Cu1–O2–Cu2, 103.7 (8).

The further transformation of $[Cu_2(UN)(O_2)]^{2+}$ (**3**) is very rapid at higher temperatures (i.e., **3** is not observable spectroscopically), and oxygenation of **1** at ≥0 °C in CH_2Cl_2 or DMF ($Cu:O_2 = 2:1$, manometry in DMF, 0 °C) quantitatively produces the green hydroxylated complex $[Cu^{II}_2(UN\text{-}O\text{-})(OH)]^{2+}$ (**4**).[18] The bond connectivity in **4** (Figure 2)[19,20] closely resembles that in the related symmetrical "parent" complex $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**5**, oxygenation product of **2**),[9] but substantial differences do exist. In **4**, the twisting of the chelating arms is such that both copper ions are on the same side of the benzene ring plane (C2–C7) and the axial pyridine ligands (N3 and N6) are on the same side of the square-based pyramidal coppers.[20] Exactly the opposite situation is true in **5**, where a pseudo-2-fold axis runs through C4,

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(15) X-ray absorption studies indicate that $[Cu_2(Nn)(O_2)]^{2+}$ (**6**) (N*n* have the same N_3 tridentates linked by variable alkane, rather than xylyl, connector groups) possess a μ-η^2:η^2 bridging peroxo–dicopper(II) moiety,[10,14] a possibility supported by the structure recently reported by Kitajima et al.[16] UV–vis spectra of **6** contain multiple and strong LMCT transitions (similar to oxy-Hc) including a prominent 340–370-nm band; the exact spectral profile is quite variable and dependent on the nature of N*n*.[10,14a,17] Other studies also indicate that the O_2 binding to **2** (and **1**) is similar to that in **6**,[10,17] i.e., a μ-η^2:η^2 peroxo structure is also suggested.

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(18) Anal. for $[Cu_2^{II}(UN\text{-}O\text{-})(OH)](PF_6)_2$ [**4-(PF_6)$_2$**]. Calcd for $C_{35}H_{38}Cu_2F_{12}N_6O_2P_2$: C, 42.38; H, 3.83; N, 8.47. Found: C, 42.09; H, 3.80; N, 8.39. UV/vis [CH_3CN; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 288 (sh, 6400), 364 (1750), 685 (270). IR (Nujol; cm^{-1}): 3590 (s, br, OH), 840 (vs, PF_6). Molar conductivity (DMF): 130.0 Ω^{-1} cm^2 mol^{-1}. An isotope labeling indicates the incorporation of >97% ^{18}O into phenol UN-OH during reaction of **1** with $^{18}O_2$.

(19) (a) X-ray quality crystals of complex $[Cu_2(UN\cdot O\text{-})(OH)](PF_6)_2$ (**4**) were obtained by recrystallization from CH_3CN/Et_2O. Complex **4-(PF_6)$_2$** crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 11.205$ (2) Å, $b = 23.261$ (5) Å, $c = 16.333$ (4) Å, $V = 4258$ (2) Å^3, and $Z = 4$. A Nicolet R3m/V diffractometer was used in the ω-scan mode to collect 3176 unique reflections, of which 1481 reflections with $F_o \geq 6\sigma|F_o|$ were useed in the solution and refinement. The positional parameters of the copper atoms were determined by the Patterson method. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were calculated and fixed at 0.96 Å from carbon. The structure was refined to the current residual values of $R = 0.088$ and $R_w = 0.686$ (Mo Kα, $\lambda = 0.710\,73$ Å). Increasing the number of observables did not improve esd's and had an adverse effect upon R factors. (b) Supplementary material.

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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 ± 0.1 μ_B/Cu vs 0.8 μ_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.

Acknowledgment. We thank the National Institutes of Health (K.D.K.; GM 28962) for support of this research.

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 (~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]

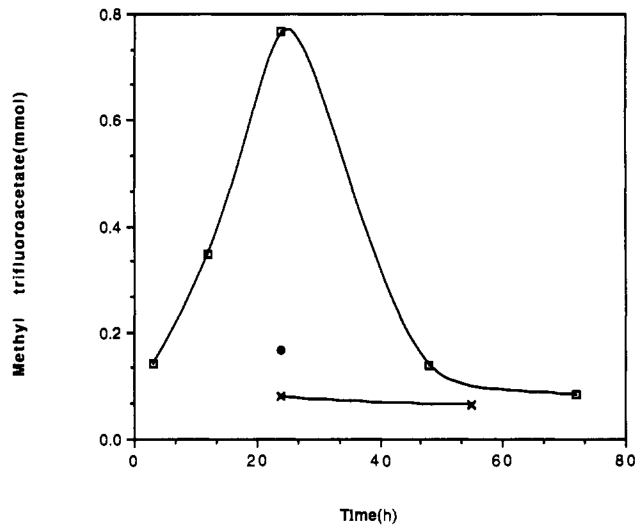


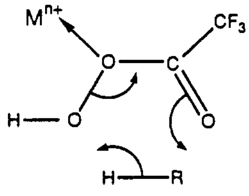
Figure 1. Yield of methyl trifluoroacetate versus time. Conditions: 90 °C, CH_4 (900 psi), $(CF_3CO)_2O$, 1.8 mL; (×) 30% H_2O_2 (2 mmol); (▣) 30% H_2O_2 (2 mmol) + $Pd(O_2CC_2H_5)_2$ (0.15 mmol); (●) 30% H_2O_2 (2 mmol) + Pd black (0.15 mmol).

We have now discovered that peroxytrifluoroacetic acid (generated from hydrogen peroxide and trifluoroacetic anhydride) oxidizes methane specifically to methyl trifluoroacetate, $CF_3CO_2CH_3$. 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 $CF_3CO_2CH_3$ 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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