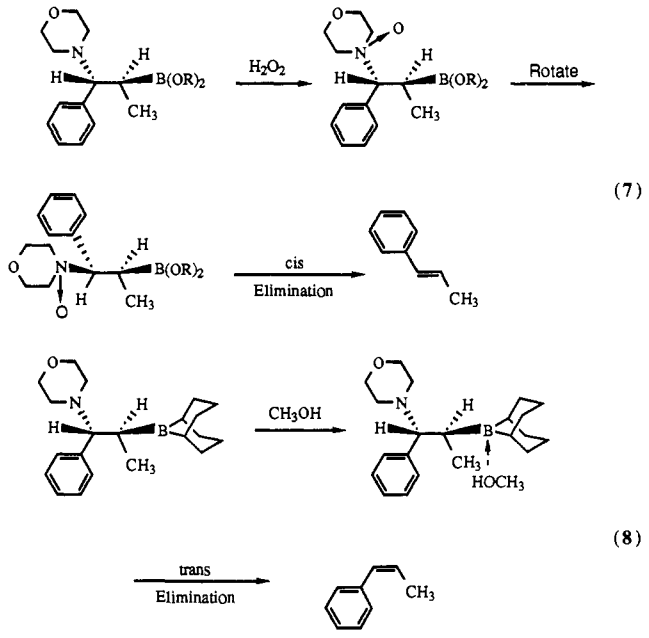
Table II. [Z]- and [E]-Alkenes from Acyclic Ketone Enamines

enamine[a]	procedure[b]	alkene[c]	yield,[d] %
[E]-1-morpholino-1-phenyl-1-propene	A	[Z]-1-phenyl-1-propene	80
	B	[E]-1-phenyl-1-propene	50
[E]-1,2-diphenyl-1-morpholinoethene	A	[Z]-1,2-diphenylethene	65
	B	[E]-1,2-diphenylethene	50
[E]-1-morpholino-1-(4-pyridyl)-1-propene	A	[Z]-1-(4-pyridyl)-1-propene	60
	B	[E]-1-(4-pyridyl)-1-propene	30
[E]-1-morpholino-1-(2-thienyl)-1-propene	A	[Z]-1-(2-thienyl)-1-propene	68
	B	[E]-1-(2-thienyl)-1-propene	45
[E]-4-pyrrolidinyl-3-heptene	A	[Z]-3-heptene[e]	69
	B[f]	[E]-3-heptene[e]	50

[a] Prepared from the corresponding ketone and morpholine in toluene. [b] (A) Hydroboration by 9-BBN followed by methanolysis. (B) Hydroboration by BMS followed by methanolysis and oxidation with alkaline hydrogen peroxide. [c] Stereochemical purity of 99% established by capillary GC and ^{13}C NMR analyses. [d] Isolated and distilled. [e] Purity established by capillary GC analysis by comparison with authentic samples purchased from the Aldrich Chemical Company. [f] Neutral hydrogen peroxide was used.

The mechanisms proposed to account for the stereochemical results are shown for [E]-1-morpholino-1-phenyl-1-propene. Hydroboration with BMS followed by methanolysis gives the corresponding dimethylboronate ester. The amino boronate ester on treatment with hydrogen peroxide affords the amine *N*-oxide which undergoes cis elimination to give [E]-1-phenyl-1-propene (eq 7). In contrast, hydroboration with 9-BBN affords the corresponding trialkylborane which on treatment with methanol undergoes a catalyzed trans elimination to produce [Z]-1-phenyl-1-propene (eq 8).



(7)

(8)

The following procedure (A) for the preparation of [Z]-1-phenyl-1-propene is representative. To a stirred suspension of 2.44 g (20.0 mmol) of solid 9-BBN in 2.0 mL of THF at 25 °C was added 4.06 g (20.0 mmol) of [E]-1-morpholino-1-phenyl-1-propene. The suspension became a clear solution after 3 h. The ^{11}B NMR spectrum of the solution indicated the absence of 9-BBN. The THF was removed at 25 °C under reduced pressure (12 Torr). The reaction flask was fitted with a distillation head, and 0.62 g (20.0 mmol) of methanol was added. A mildly exothermic reaction occurred, and the reaction mixture solidified. Upon heating, the solid melted, and 1.90 g (81% yield) of isomerically pure [Z]-1-phenyl-1-propene, bp 62-64 °C (12 Torr), was obtained by distillation. The same procedure is applicable to the preparation of alkenes and dienes from aldehyde enamines.

The following procedure (B) for the preparation of [E]-1-phenyl-1-propene is representative. To a 1.0 M solution of [E]-1-morpholino-1-phenyl-1-propene in THF at 25 °C was added 2.0 mL (20.0 mmol) of 10.0M BMS with stirring. The reaction was stirred at 25 °C for 1 h and then methanolized. The resulting boronic ester was purified by distillation: bp 116-118 °C (0.25 Torr), 80% yield. The boronic ester was oxidized by using solid sodium hydroxide and 30% hydrogen peroxide to give a 50% yield (GLC) of isomerically pure [E]-1-phenyl-1-propene which was purified by distillation: bp 72-74 °C (20 Torr).

Chemoselective Enzymatic Monoacylation of Bifunctional Compounds

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The selective monoprotection of a given function in a heterofunctional molecule constitutes a challenging task in organic synthesis.[1] In particular, it would be highly desirable to have the flexibility of directing the position of monoprotection simply by varying the modifying agent. Recently, the hydrolytic enzymes lipases and proteases have been successfully employed for selective monoacylation of diols[2] and sugars[3] in organic solvents. In the present study, we have found that in heterofunctional compounds, such as aminoalcohols, the chemoselectivity of enzymatic acylation can be readily controlled by the nature of the acyl moiety.

6-Amino-1-hexanol (**1**) was selected as a model bifunctional compound. In the reaction between this aminoalcohol and 2-chloroethyl butyrate (100 mM each, *tert*-amyl alcohol as a solvent, 45 °C), catalyzed by 100 mg/mL *Aspergillus niger* lipase,[4] the initial rate of enzymatic acylation of the OH group was 37 times

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(1) McOmie, J. F. W. *Protective Groups in Organic Chemistry*; Plenum: London, 1973. Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981.

(2) Cesti, P.; Zaks, A.; Klibanov, A. M. *Appl. Biochem. Biotechnol.* **1985**, *11*, 401-407. Ramos Tombo, G. M.; Schar, H.-P.; Fernandez, X.; Ghisalba, O. *Tetrahedron Lett.* **1986**, *27*, 5707-5710. Hemmerle, H.; Gais, H.-J. *Tetrahedron Lett.* **1987**, *28*, 3471-3474. Cantacuzene, D.; Guerreiro, C. *Tetrahedron Lett.* **1987**, *28*, 5153-5156. Wang, Y.-F.; Wong, C.-H. *J. Org. Chem.* **1988**, *53*, 3127-3129. Riva, S.; Klibanov, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 3291-3295.

(3) (a) Therisod, M.; Klibanov, A. M. *J. Am. Chem. Soc.* **1986**, *108*, 5638-5640. (b) Therisod, M.; Klibanov, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 3977-3981. (c) Riva, S.; Chopineau, J.; Kieboom, A. P. G.; Klibanov, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 584-589.

(4) *Aspergillus niger* lipase (lipase K-30, lot no. LPJ04508) and *Pseudomonas* sp. lipoprotein lipase (LPL lot no. LPL04512) were purchased from Amano International Enzyme Co. (Troy, VA). Porcine pancreatic lipase (Lot No. 74F0470) was obtained from Sigma Chemical Co. (St. Louis, MO). All lipases were suspended in the reaction media without any pretreatment.

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Table I. Chemoselective Enzymatic Acylation of Aminoalcohols in *tert*-Amyl Alcohol[a,b]

acylating agent (mmol)	aminoalcohol (mmol)	enzyme	bond formed	product[c]	isolated yield, %
ButOEtCl (18)	6-amino-1-hexanol (15)	lipase	C–O	$ButO(CH_2)_6NH_2$[d]	47
N-Ac-L-Phe-OEtCl (8.4)	6-amino-1-hexanol (7)	subtilisin Carlsberg	C–N	*N*-Ac-L-Phe-$NH(CH_2)_6$-OH[e]	74
ButOEtCl (18)	*trans*-4-aminocyclohexanol (15)	lipase	C–O		42
N-CBZ-L-Tyr-OEtCl (20)	L-Thr-NH_2 (20)	subtilisin Carlsberg	C–N	*N*-CBZ-L-Thr-L-Thr-NH_2[g]	73
N-CBZ-L-Thr-OEtCl (20)	L-Thr-OEtCl (20)	subtilisin Carlsberg	C–N	*N*-CBZ-L-Thr-L-Thr-NH-Ind[h]	81
N-Ac-D-Ala-OEtCl (3.7)	L-Ser-NH-Nph (3.7)	subtilisin BPN′	C–N	*N*-Ac-D-Ala-L-Ser-NH-Nph[i]	64

[a] The amounts of the substrates given in the first two columns were dissolved in *tert*-amyl alcohol (150, 70, 150, 200, 200, and 37 mL, respectively, in the order of entries from top to bottom). Then 100 mg/mL *Aspergillus niger* lipase[4] or 2 mg/mL subtilisin[6] was added, and the suspension (enzymes are insoluble in *tert*-amyl alcohol[7]) was shaken at 250 rpm and 45 °C. After a certain period of time (indicated below) the reaction was stopped by filtering out the enzyme, the solvent was evaporated under vacuum, and the residue was washed with water (the Tyr–Thr and Thr–Thr dipeptides) or ethyl acetate (the third and last entries) and then recrystallized from MeOH if possible. In the case of the first and second entries, the products were purified by silica gel column chromatography using butanol–water–acetic acid (4:1:0.4) and methylene chloride–methanol (23:2), respectively, as a solvent. Nonstandard abbreviations used: But – butyryl, Ind – indolinyl, and Nph – β-naphthyl. [b] *tert*-Amyl alcohol was of analytical grade and used without further purification apart from drying with Linde's 3Å molecular sieves. [c] All isolated products were pure by ^1H NMR, TLC, and HPLC or GC. The 250 MHz ^1H NMR spectra for all products were consistent with their proposed structures. It should be noted that in no case was any appreciable reaction observed without enzymes under the conditions used. [d] After 24 h, 7.05 mmol of the oily product was obtained. The product was identical with the chemically synthesized compound[5] by GC and TLC. GC–MS, *m/e* 188 (5), 116 (13), 101 (7), 101 (100), 89 (62), 86 (14), 83 (6), 82 (7), 81 (7), 73 (6), 72 (10), 71 (46), 70 (12), 69 (9), 67 (8), 65 (5), 57 (6), 56 (50), 55 (45), 54 (9), 53 (5). [e] After 21 h, 5.18 mmol of the crystalline product (mp 134–136 °C) was obtained. Anal. Calcd for $C_{17}H_{26}N_2O_3$: C, 66.63; H, 8.55; N, 9.14. Found: C, 66.90; H, 8.57; N, 8.93. [f] After 2 days, 6.3 mmol of the oily product was obtained. Anal. Calcd for $C_{10}H_{19}O_2N$: C, 64.85; H, 10.27; N, 7.56. Found: C, 64.59; H, 10.10; N, 7.30. [g] After 2.5 days, 14.6 mmol of the crystalline product (mp 204–206 °C) was obtained. $[\alpha]^{25}_D$ −3.3° (*c* 0.9, MeOH). Anal. Calcd for $C_{21}H_{25}N_3O_6$: C, 60.72; H, 6.02; N, 10.12. Found: C, 60.35; H, 6.38; N, 9.84. [h] After 2.5 days, 16.2 mmol of the crystalline product (mp 98–100 °C) was obtained. $[\alpha]^{25}_D$ −37.0° (*c* 0.3, MeOH). Anal. Calcd for $C_{25}H_{31}N_3O_6$: C, 63.95; H, 6.65; N, 8.95. Found: C, 63.79; H, 6.48; N, 9.03. [i] After 3.5 days, 2.36 mmol of the crystalline product (mp 222 °C dec) was obtained. $[\alpha]^{25}_D$ −74.9° (*c* 0.3, MeOH). Anal. Calcd for $C_{18}H_{21}O_4N_3$: C, 62.97; H, 6.12; N, 12.24. Found: C, 62.79; H, 6.08; N, 12.10.

greater than that of the NH_2 group.[5] In contrast, when the same ester of *N*-acetyl-L-phenylalanine was used as the acylating agent, the reactivity of the hydroxyl group in the enzymatic coupling was less than one fifth of that of the amino group. This surprising reversal of chemoselectivity was also observed with other biocatalysts such as porcine pancreatic lipase and *Pseudomonas* sp. lipoprotein lipase: in the case of the aliphatic ester acylation of the OH group in **1** was 25 and 62 times, respectively, faster than that of the NH_2 group, whereas for the Phe substrate the reactivity of the amino group in **1** was more than 50 and 10 times, respectively, greater than that of its hydroxyl counterpart.

The next step was to develop a selective, preparative enzymatic acylation of either the OH group or NH_2 group of this bifunctional compound depending on the acylating agent employed. The first entry in Table I depicts lipase-catalyzed synthesis of *O*-butyryl-**1** on a mmol scale. The N-acylation with *N*-Ac-L-Phe-OEtCl catalyzed by lipases was much slower than the O-acylation, thereby making the preparative conversion less attractive. Fortunately, we observed that another hydrolase, the protease subtilisin Carlsberg,[6] was extremely reactive in this process, while still exhibiting a 50-fold preference toward the NH_2 over the OH group. Therefore, this enzyme was employed instead of lipase for the preparative N-acylation of **1** (second entry in Table I).

It is noteworthy that lipase-catalyzed acylation of **1** occurs with chemoselectivity opposite to that of the chemical reaction: incubation of the aminoalcohol with butyryl chloride (200 mM each) in *tert*-amyl alcohol at 45 °C for 3 h resulted, expectedly, in the nearly quantitative acylation of the NH_2 group exclusively.[5] This chemoselectivity was not limited to **1**: as shown in Table I, *trans*-4-aminocyclohexanol was O-butyrylated on a preparative scale with *Aspergillus niger* lipase as a catalyst, as evidenced by ^1H NMR.[8] In addition, the nucleoside adenosine was butyrylated by subtilisin in dimethylformamide exclusively at the OH group,[3c] while the chemical acylation of such compounds occurs only at the NH_2 group.[9]

The aforedescribed NH_2-chemoselectivity of subtilisin when acylating with *N*-Ac-L-Phe-OEtCl was found to be rather general with respect to both the amino acid in the acylating agent and the nucleophile molecule. Consequently, derivatives of hydroxy amino acids could be enzymatically acylated without the need for protection of OH groups. As an illustration, we utilized both subtilisin Carlsberg and BPN′ to prepare dipeptide fragments of the octapeptide T which had been reported[10] to possess anti-AIDS-virus activity. The last three entries in Table I indicate that the subtilisins catalyzed formation[11] of only the natural peptide bond.[12]

(5) The direction of acylation was established by gas chromatography using authentic, chemically synthesized mono-O-, mono-N-, and di-O,N-butyrylated **1**. The last two compounds were prepared according to a general method (Onodera, K.; Kitaoka, S. *J. Org. Chem.* **1960**, *25*, 1322–1325) by acylation with equimolar butyric anhydride in THF and a 2-fold molar excess of butyryl chloride in the presence of pyridine in THF, respectively. Mono-O-butyrylated **1** was prepared by using a general methodology (Bodanszky, M. *Principles of Peptide Synthesis*; Springer: Berlin, 1984; p 90) consisting of protection of the NH_2 group by carbobenzoxylation and acylation of the OH group by butyryl chloride in the presence of pyridine in THF, followed by deprotection of the NH_2 group via catalytic hydrogenation. All compounds were positively identified by ^1H NMR.

(6) Subtilisin Carlsberg (protease from *Bacillus subtilis*, type VIII) and subtilisin BPN′ (protease from *Bacillus amyloliquefaciens*, type XXVII) were purchased from Sigma. Both enzymes were "pH-adjusted" (i.e., freeze-dried from aqueous solution of the pH optimal for enzymatic activity) to enhance their reactivity in organic solvents.[7]

(7) Zaks, A.; Klibanov, A. M. *J. Biol. Chem.* **1988**, *263*, 3194–3201.

(8) We found that shorter aliphatic aminoalcohols, e.g., 2-aminoethanol and 4-amino-1-butanol, were also enzymatically butyrylated at the OH group but subsequently underwent nonenzymatic O→N migration of the acyl moiety (Winstein, S.; Boschan, R. *J. Am. Chem. Soc.* **1950**, *72*, 4669–4677. Lemieux, R. U. In *Molecular Rearrangements*; de Mayo, P., Ed.; Interscience: New York, 1964; Part 2, pp 709–769. Horton, D. In *The Amino Sugars*; Jeanloz, R. W., Ed.; Academic Press: New York, 1969; Vol IA, pp 1–211). This migration may be responsible for a recently reported (Goter, V.; Brieva, R.; Rebolledo, F. *J. Chem. Soc., Chem. Commun.* **1988**, 957–958) N-acetylation of 1,2-aminoalcohols catalyzed by porcine pancreatic lipase in ethyl acetate.

(9) E.g., see: Watanabe, K. A.; Fox, J. J. *Angew. Chem.* **1966**, *78*, 589.

(10) Barnes, D. M. *Science* **1987**, *237*, 128–130. Ruff, M. R.; Martin, B. M.; Ginns, E. I.; Farrar, W. L.; Pert, C. B. *FEBS Lett.* **1987**, *211*, 17–22.

(11) Margolin, A. L.; Tai, D.-F.; Klibanov, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 7885–7885.

(12) Structure elucidation was achieved by means of 250 MHz ^1H NMR with DMSO-d_6 as a solvent. For all three peptides, the NMR spectra were consistent with exclusively peptide (rather than ester) bond formation between the amino acid residues. For instance, in the case of *N*-CBZ-L-Thr-L-Thr indolinylamide (i) the two hydroxyl group protons resonate as doublets (4.87 and 4.98 ppm), and (ii) the corresponding methine protons (3.91 and 3.99 ppm) show no downfield shift as would have been expected for the ester bond. Analogous data were obtained for the other two peptides.

The ability to control the chemoselectivity of enzymatic modification, apart from its synthetic value for aminoalcohols, if understood mechanistically (currently under investigation), might be extendable to other heterofunctional compounds.

(13) This work was financially supported by Grant GM39794 from the National Institutes of Health. We are grateful to Professor Thorleif Anthonsen (University of Trondheim, Norway) for helpful discussions. The Thr-Thr dipeptide was synthesized by Dr. Dar-Fu Tai.

Dioxygen-Copper Reactivity. Comparisons of the Reactions of Electrophiles and Other Reagents with Three Classes of Peroxo-Dicopper(II), $\{Cu_2-O_2\}^{n+}$, Species

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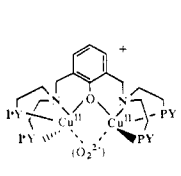
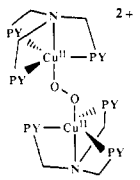
We have recently described three types of peroxo-dicopper(II) complexes, $\{Cu_2-O_2\}^{n+}$ (**1-3**, n = 1 or 2, PY = 2-pyridyl), which



1



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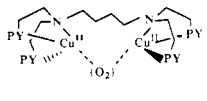

3

are formed reversibly by the addition of O_2 to either mono- or dinuclear copper(I) complexes at -80 °C in solution. $[Cu_2(XYL-O-)(O_2)]^+$ (**1**), contains an unsymmetrically bound peroxo ligand (ν_{O-O} = 803 cm^{-1}) in a phenoxo-bridged dicopper(II) unit.[1] The X-ray crystal structure of **2** features a trans μ-1,2-peroxo ligand bound to Cu(II) ions in $[(LCu)_2-(O_2)]^{2+}$ (L = tris[(2-pyridyl)methyl]amine).[2] We have also described a series of $\{Cu_2-O_2\}^{2+}$ complexes such as $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**), which possess tridentate nitrogen donor groups connected by various hydrocarbon units.[3] In order to provide insights into the structures of **1-3** and the nature (e.g., nucleophilic or electrophilic) of the bound dioxygen (peroxo) ligands, we are carrying out a series of reactivity studies. Here, we report preliminary results of reactions of complexes **1-3** with the reagents SO_2, CO_2, H^+, $ArC(O)^+$, PPh_3, and PhMgBr. We find that **1** and **2** react like other M_n-O_2 complexes which have a basic or nucleophilic peroxo moiety;[4] however, **3** behaves otherwise.

Sulfur dioxide and carbon dioxide are electrophilic reagents commonly used in reactivity studies involving metal-dioxygen species.[4] The $\{Cu_2-O_2\}^{n+}$ complexes (**1-3**) all react at -80 °C with SO_2 to give sulfato-containing dicopper(II) compounds.[5] However, with respect to addition of CO_2, dioxygen-copper complex **3** behaves differently than **1** or **2**, and there is no reaction. Carbon dioxide reacts with the latter leading to the formation of carbonato complexes. Thus, addition of $CO_{2(g)}$ to **1** at -80 °C in CH_2Cl_2 causes the loss of the characteristic 505-nm band[1] producing a green (λ_{max} = 340 nm (ϵ = 3700) and 400 nm (ϵ = 3800)) solution, presumed to contain a peroxycarbonato species.[6] Either via thermal decomposition or by reaction of this solution with PPh_3 (producing O=PPh_3), a μ-CO_3^{2-} complex, $[Cu_2(XYL-O-)(CO_3^{2-})]^+$, is formed.[7]

$$Cu^{II}_2(O_2^{2-}) + CO_2 \rightarrow Cu^{II}_2(CO_4^{2-}) + \text{warming} \rightarrow Cu^{II}_2(CO_3^{2-})$$

$$Cu^{II}_2(O_2^{2-}) + CO_2 \rightarrow Cu^{II}_2(CO_4^{2-}) + PPh_3 \rightarrow Cu^{II}_2(CO_3^{2-}) + O{=}PPh_3$$

A similar behavior is observed with **2**, and reaction with CO_2 (-80 °C) causes bleaching of the characteristic bands at 525 and 590 nm. The resulting solution reacts with PPh_3 to give O=PPh_3 (97% conversion) and $[(LCu^{II})_2(CO_3^{2-})]^{2+}$.[8] The structure[9,10] of this complex (Figure 1) shows that it contains a bridged-bidentate carbonato group in a dinuclear unit, with each copper(II) ion in a distorted square-pyramidal geometry (axial pyridine N3 and N7).[11,12] This is a somewhat unusual geometry for Cu(II) complexes of L, which normally are found in trigonal bipyramidal coordination.[2]

In reactions with H^+, the dioxygen ligands in **1** and **2** are readily protonated. Addition of 1 mol-equiv of HBF_4 or HPF_6 at -80 °C to **1** gives a hydroperoxo-dicopper(II) complex, $[Cu_2(XYL-O-)(OOH)]^{2+}$.[13] With 2 or more equiv, H_2O_2 is produced in 88%

(1) (a) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 2668-2679. (b) Pate, J. E.; Cruse, R. W.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 2624-2630. (c) Blackburn, N. J.; Strange, R. W.; Cruse, R. W.; Karlin, K. D. *J. Am. Chem. Soc.* **1987**, *109*, 1235-1237.

(2) Jacobson, R. R.; Tyeklar, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 3690-3692, and references cited therein.

(3) (a) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Meyer, G. J.; Farooq, A.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 1196-1207, and references cited therein. (b) Blackburn, N. J.; Strange, R. W.; Farooq, A.; Haka, M. S.; Karlin, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 4263-4272.

(4) (a) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1. (b) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

(5) The sulfato complexes produced, recrystallized, and characterized are $[Cu_2(XYL-O-)SO_4]PF_6 \cdot 0.25CH_2Cl_2$ (70% yield): Anal. Calcd for $C_{36.25}H_{39.5}Cl_{0.5}Cu_2F_6N_6O_5PS$: C, 45.30; H, 4.14; N, 8.68. Found: C, 44.94; H, 4.24; N, 8.68: IR (Nujol) ν (SO) = 1230 (s), 1130 (vs), 970 (s) cm^{-1}. $[(LCu)_2(SO_4)](PF_6)_2$ (59% yield): Anal. Calcd for $C_{36}H_{36}Cu_2F_{12}N_8O_4P_2S$: C, 39.53; H, 3.52; N, 10.24. Found: C, 40.39; H, 3.59; N, 10.15: IR (Nujol) ν (SO) = 1220 (s), 1125 (s), 1000 (s) cm^{-1}. $[Cu_2(N4PY2)(CH_3CN)_2](SO_4)(PF_6)_2 \cdot Et_2O$ (54% yield): Anal. Calcd for $C_{40}H_{56}Cu_2F_{12}N_8O_5P_2S$: C, 40.78; H, 4.79; N, 9.51. Found: C, 41.03; H, 4.69; N, 9.77: IR (Nujol) ν (SO) = 1100 (br) cm^{-1}.

(6) Examples of $M-O_2$ systems reacting with CO_2 to form peroxycarbonato species are as follows: (a) Hayward, P. J.; Blake, D. M.; Wilkinson, G.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5873. (b) Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5832. (c) Schappacher, M.; Weiss, R. *Inorg. Chem.* **1987**, *26*, 1190-1192.

(7) $[Cu_2(XYL-O-)CO_3]PF_6 \cdot 0.5\ CH_2Cl_2$ (87% yield): Anal. Calcd for $C_{37.5}H_{40}ClCu_2F_6N_6O_4P$: C, 47.62; H, 4.23; N, 8.88. Found: C, 47.96; H, 4.32; N, 9.12. IR (Nujol) ν (CO) = 1535 (m), cm^{-1}.

(8) $[L_2Cu_2(CO_3)](ClO_4)_2$ (84% yield): Anal. Calcd for $C_{37}H_{36}Cl_2Cu_2N_8O_{11}$: C, 45.97; H, 3.75; N, 11.59. Found: C, 45.94; H, 3.68; N, 11.61. IR (Nujol) ν (CO) = 1520 (s), 1340 (vs), 880 (m), 690 (m) cm^{-1}. μ_{RT} = 1.37 μ_B/Cu.

(9) $[(LCu)_2(CO_3)](ClO_4)_2 \cdot (CH_3CH_2CN)_2$ crystallizes in the triclinic space group $P\bar{1}$ with a = 13.174 (3) Å, b = 13.994 (4) Å, c = 13.978 (4) Å, α = 108.08 (2)°, β = 92.01 (2)°, γ = 101.49 (2)°, V = 2387 (1) Å^3, and Z = 2. A Nicolet R3m/V diffractometer was used in the ω-scan mode to collect 6544 unique reflections of which 3569 reflections with $F_o \geq 6\sigma|F_o|$ were used 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 for carbon. Anisotropic refinement was carried out on all non-hydrogen atoms of the cation and chlorine atoms in the anions; two molecules of lattice propionitrile per dinuclear unit were identified and located in the final stages of refinement (some disorder is seen for one anion). The structure was refined to the current residual values of R = 0.0748 and R_w = 0.0775 (Mo Kα,λ = 0.71073 Å). For some atoms, the U's are peculiarly anisotropic (Table IV, Supplementary Material); these may be a result of 30% crystal decomposition which was indicated by the decrease in average intensity of three check reflections monitored during data collection.

(10) Supplementary Material.

(11) References to complexes with a similarly coordinated carbonato group are as follows: (a) Gagne, R. R.; Gall, R.; Lisensky, G. C.; Marsh, R. E.; Speltz, L. M. *Inorg. Chem.* **1979**, *18*, 771-781. (b) Churchill, M. R.; Lashewycz, R. A.; Koshy, K.; Dasgupta, T. P. *Inorg. Chem.* **1981**, *20*, 376. (c) Healey, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1913.

(12) Dinuclear bridging tridentate carbonato coordination to Cu(II) is also common: (a) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Hutchinson, J. P. *Inorg. Chem.* **1982**, *21*, 1002-1007, and references cited therein. (b) Davis, A. R.; Einstein, F. W. B. *Inorg. Chem.* **1980**, *19*, 1203-1207.

0002-7863/89/1511-0388$01.50/0