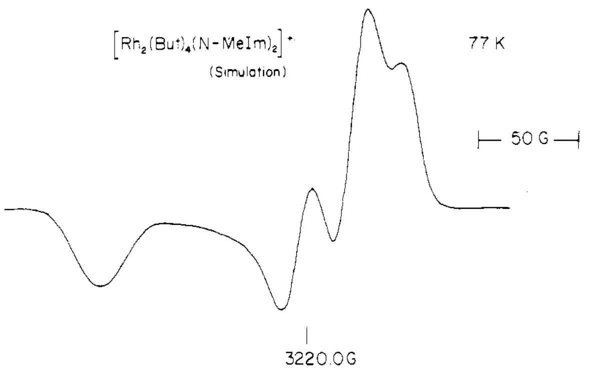

Figure 7. Simulation of the EPR spectrum of [Rh$_2$(But)$_4$(*N*-MeIm)$_2$]$^+$.

maximum intensity shown, the sample was lowered to liquid-nitrogen temperature. The 77 K spectrum is shown in Figure 6. Unlike the phosphorus case, the spectrum contains three *g* values. Simulation for the *N*-methylimidazole compound gives $g_x = 1.997$, $g_y = 2.017$, and $g_z = 2.091$. The simulated spectrum is shown in Figure 7. The rhodium and/or nitrogen hyperfine interactions are unresolved. Similar results were obtained with pyridine.

The three-*g*-value spectrum conclusively shows that the *N*-methylimidazole adduct does not have axial symmetry. It is clear that the highest lying orbital is not similar to that found for the bis(phosphorus) complex. Both pyridine (a π-interacting base) and *N*-MeIm (a non-π-interacting base) give three-*g*-value spectra as opposed to the axial spectra of the phosphorus bases. We suspect that the species formed in the case of pyridine and *N*-methylimidazole have monodentate butyrate with the vacated coordination sites occupied by these donors. Only by disrupting the bridging carboxylate framework can there be such a decidedly nonaxial system. There is precedence for this type of reaction for rhodium trifluoroacetate.[12]

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Cu$_2$(*o*-Ph$_2$PC$_6$H$_4$C(O)CHC(O)C(CH$_3$)$_3$)$_2$: Synthesis, Structure, and Ligand Oxygenation to a Mixed-Valence Cu(I)–Cu(II) Complex

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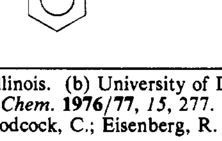
The synthesis of (*o*-(diphenylphosphino)benzoyl)pinacolone (HacacP) is described. The complexes M$_2$(acacP)$_2$ (M = Cu, Ag) were synthesized from the reaction of HacacP, NEt$_3$, and Cu(CH$_3$CN)$_4$ClO$_4$ or AgClO$_4$. Treatment of a CH$_2$Cl$_2$ solution of Cu$_2$(acacP)$_2$ (**1**) with molecular oxygen gave Cu$_2$(acacP)$_2$(μ-*o*-O$_2$CC$_6$H$_4$P(O)Ph$_2$) (**2**), which can also be prepared by treatment of **1** with Cu(*o*-Ph$_2$P(O)C$_6$H$_4$CO$_2$)$_2$ and HacacP. After demetalation the organic products of the oxygenation were found to consist of equal amounts of *o*-Ph$_2$P(O)C$_6$H$_4$CO$_2$H and *t*-BuCO$_2$H, which were derived from acacP$^-$. The crystal structure and molecular geometry of Cu$_2$(acacP)$_2$(*o*-O$_2$CC$_6$H$_4$P(O)Ph$_2$) has been determined by X-ray diffraction: $P\bar{1}$, $a = 13.592$ (4) Å, $b = 14.913$ (5) Å, $c = 18.501$ (5) Å, $\alpha = 85.78$ (3)°, $\beta = 86.19$ (2)°, $\gamma = 72.61$ (2)°, $Z = 2$, $\mu = 7.17$ cm^{-1} (Mo Kα). The crystal structure and molecular geometry of [Cu(acacP(O))(OCH$_3$)]$_2$·2CH$_3$OH have been determined by X-ray diffraction: $P2_1/n$, $a = 9.750$ (2) Å, $b = 16.399$ (3) Å, $c = 16.698$ (4) Å, $\beta = 97.25$ (2)°, $Z = 2$, $\mu = 9.17$ cm^{-1} (Mo Kα).

Introduction

The rarity of bimetallic coordination compounds where *both* metals are reactive contrasts sharply with the variety of bimetallic complexes that are chemically dormant.[2] In recent years this deficiency has been addressed through reactivity studies on A-frame complexes of bis(phosphine) ligands[3] and complexes of face-to-face porphyrins.[4] Our contribution to this area follows from work with the "compartmentalized" phosphine β-diketone, (*o*-(diphenylphosphino)benzoyl)pinacolone, HacacP.[5]



As expected for a ligand of its complexity, acacP$^-$ can bind two metals in a variety of ways. The simplest and, structurally, the most unusual of its bimetallic derivatives is Cu$_2$(acacP)$_2$ (**1**), which consists of two cofacially arrayed 3-coordinate copper(I) centers (Figure 1). Compound **1** has a rich chemistry: it undergoes 1-electron oxidative addition,[6] it reversibly binds *o*-quinones,[7] and it reacts readily with molecular oxygen. In this report we describe the preparation of HacacP, **1**, and the products formed upon oxygenation of **1**. Copper-catalyzed substrate oxygenation is an important biochemical process,[8] and it is only very recently that Karlin,[9] Rogič,[10] and others have demonstrated the hydroxylation of an aromatic ring through studies on synthetic complexes.

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0020-1669/84/1323-3124$01.50/0

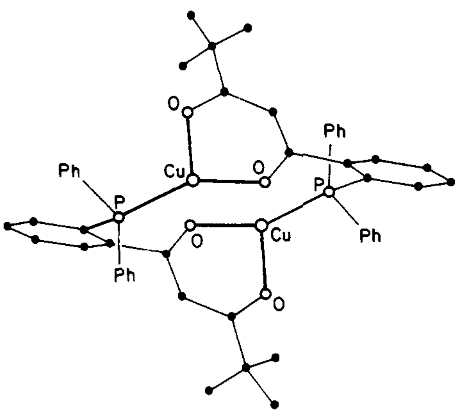

Figure 1. Ball and stick drawing of $Cu_2(acacP)_2$ (**1**).

Experimental Section

Materials and Methods. All compounds described herein are air-stable in the solid state. Syntheses were routinely conducted by using Schlenk techniques, and workups were done aerobically in an efficient hood. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and pinacolone was distilled from $CaSO_4$. All other reagent grade chemicals were used without further purification. Diazomethane was generated from Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) for large-scale (>10 mmol) preparations and from MNNG (*N*-methyl-*N'*-nitro-*N*-nitrosoguanidine) for small-scale (<1 mmol) preparations; both reagents were purchased from Aldrich Chemical Co. $Cu(MeCN)_4ClO_4$,[11] $Cu(O_2CC_6H_4P(O)Ph_2)_2$,[12] and *o*-(diphenylphosphino)benzoic acid[13] were prepared according to published procedures.

The following instruments were used in this work: IR, Perkin-Elmer 599B; UV–vis, Varian Cary 219; 90-MHz ^1H NMR, Varian EM-390 (with internal frequency lock); 40.5-MHz ^{31}P NMR, Varian XL-100 (internal ^2H frequency lock, positive δ downfield of external standard 85% H_3PO_4); X-band EPR, Varian E-9 (calibration standard DPPH, 9.1715 GHz); gas chromatography, Hewlett-Packard 5730A with thermal conductivity detector, Spherocarb column (3 ft), Analabs or Tracor 560 with flame ionization detector, 3% OV-225 on 100/120 ChrW-HP column (6 ft); digital capacitance monometer MKS "Baratron" 1000-torr 310BHS sensor head with digitial offset and 4 $^1/_2$ digital readout. Field desorption (FD) mass spectra were measured as a service on a Varian 731 spectrometer at the Mass Spectrometry Laboratory. Elemental analysis data were obtained from the University of Illinois Microanalytical Laboratory.

***o*-(Diphenylphosphino)methylbenzoate, *o*-$Ph_2PC_6H_4CO_2CH_3$.** A ~2.9 M solution of CH_2N_2 in ether (500 mL, 0.143 mol) was added dropwise to a solution of *o*-$Ph_2PC_6H_4CO_2H{\cdot}CH_3OH$ (26 g, 0.077 mol) in Et_2O (800 mL). After the addition, the yellow color was discharged with glacial acetic acid (ca. 3 mL). The resulting solution was concentrated sixfold and was diluted with MeOH (100 mL), concentrated further (to 125 mL), and cooled. The yield of white crystalline product was 86% (21.1 g), mp 96–97 °C. IR (mull) ν_{CO} 1712 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.6–6.9 (m, 14 H), 3.70 (s, 3 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) –5.1 ppm. Anal. Calcd for $C_{20}H_{17}O_2P$: C, 75.00; H, 5.35; P, 9.67. Found: C, 75.00; H, 5.32; P, 9.70.

(*o*-(Diphenylphosphino)benzoyl)pinacolone, *o*-$Ph_2PC_6H_4C(O)$-$CH_2C(O)$-*t*-Bu (HacacP). Pentane-washed 35% KH–oil dispersion (500 mg, 12.4 mmol) was slurried in THF (20 mL). To this was added pinacolone (500.8 mg, 5.0 mmol) in THF (10 mL) dropwise. After the vigorous H_2 evolution had subsided (~10 min), a solution of *o*-$PH_2PC_6H_4CO_2Me$ (1.6 g, 5 mmol) in THF (15 mL) was added and the resulting solution was heated under reflux for 8 h. The cooled orange reaction mixture was cautiously poured into water (135 mL) and acidified with dilute HCl to pH 4 (60 mL of 0.2 M HCl). The yellow product was extracted with CH_2Cl_2 (3 × 50 mL portions), dried over Na_2SO_4, and concentrated eightfold. The crude yellow product was precipitated with methanol and recrystallized from hot methanol. Upon cooling, a 66% yield (1.85 g) of cream-colored crystals was obtained, mp 118 °C. IR (mull) ν_{CO} 1605 (s), 1580 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 14.8 (br s, 1 H), 7.7–6.8 (m, 14 H), 5.87 (s, 1 H), 1.09 (s, 9 H); $^{31}P\{^1H\}$ NMR, –9.0 ppm. Anal. Calcd for $C_{25}H_{25}O_2P$: C, 77.32; H, 6.44; P, 7.99. Found: C, 77.22; H, 6.56; P, 8.02.

$Cu_2(acacP)_2$ (1). $[Cu(MeCN)_4]ClO_4$ (820 mg, 2.5 mmol) and HacacP (970 mg, 2.5 mmol) were dissolved in MeCN (35 mL). Upon addition of NEt_3 (350 μL, 2.5 mmol), a yellow microcrystalline product was deposited. This product was filtered under nitrogen and washed with water (60 mL), 95% EtOH (30 mL), and Et_2O (8 mL); yield 92% (1.0392 g). IR (mull) ν_{CO} 1571 (s), 1548 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.5–7.1 (m, 14 H), 5.18 (s, 1 H), 0.88 (s, 9 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) –3.6 ppm; FDMS, *m/z* 900 (M^+). Anal. Calcd for $C_{50}H_{48}Cu_2O_4P_2$: C, 66.59; H, 5.33; Cu, 14.10; P, 6.88. Found: C, 66.64; H, 5.28; Cu, 14.10; P, 6.91.

$Ag_2(acacP)_2$. HacacP (194 mg, 0.5 mmol) and $AgClO_4$ (103.7 mg, 0.5 mmol) were dissolved in MeCN (40 mL). After the addition of NEt_3 (70 μL, 0.5 mmol), a cream-colored microcrystalline product was deposited. The filtered product was washed with water (5 mL), 95% EtOH (5 mL), and Et_2O (5 mL) and dried in vacuo at room temperature; yield 57% (140.5 mg). The product is moderately light sensitive. IR (mull) ν_{CO} 1595 (s), 1565 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6–7.3 (m, 14 H), 5.42 (s, 1 H), 0.98 (s, 9 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) +8.4 ppm [$^1J(^{109}Ag,^{31}P)$ = 826 Hz, $^1J(^{107}Ag,^{31}P)$ = 718 Hz]; FDMS, *m/z* 990 (M^+). Anal. Calcd for $C_{50}H_{48}Ag_2O_4P_2$: C, 60.60; H, 4.85; P, 6.26. Found: C, 60.25; H, 4.84; P, 6.48.

Oxygenation of $Cu_2(acacP)_2$ (1). A yellow solution of $Cu_2(acacP)_2$ (100 mg, 0.11 mmol) in CH_2Cl_2 (100 mL) was stirred under 40 psig of O_2 for 24 h. Methanol was added to the green solution to give impure crystals upon concentration. Analytically pure product was obtained by chromatography of a CH_2Cl_2 solution of the green product on a 3 × 48 cm S-X 4 Biobeads column. Three fractions were taken from the green band. The first was diluted with methanol, affording analytically pure $Cu_2(acacP)_2(\mu\text{-}o\text{-}Ph_2POC_6H_4CO_2)$. IR (mull) ν_{CO} 1566 (s), 1541 (s), 1505 (s), 1425 (vs), 1400 (vs), ν_{PO} 1168 (s) cm^{-1}; EPR (1:1 (v:v) CH_2Cl_2:toluene, –196 °C) $g_{\parallel}$ = 2.286, $g_{\perp}$ = 2.067, $A_{\parallel}$ = 494 MHz, $A_{\perp}$ = 40 MHz. Anal. Calcd for $C_{69}H_{62}Cu_2O_7P_3$: C, 67.75; H, 5.07; Cu, 10.40; P, 7.61. Found: C, 67.84; H, 5.07; Cu, 10.15; P, 7.93.

Analysis of Organic Acids Formed upon Oxygenation of $Cu_2(acacP)_2$ (1). A solution of **1** (200 mg, 0.222 mmol) in CH_2Cl_2 (50 mL) was heated at 40 °C under 40 psig of O_2 for 16 h. Mesitylene (7.7 μL, 0.0555 mmol) was added as an internal standard. The green solution was concentrated and treated with CH_3SH, and the precipitated $[Cu(SCH_3)]_n$ was removed by filtration through Celite. The resulting pale yellow solution was concentrated to a small volume in vacuo and dissolved in $CDCl_3$ (~2 mL). The $CDCl_3$ solution was treated with CH_2N_2 in a microscale reactor. After purging with N_2, the solution was analyzed by ^1H NMR, which established the presence of *o*-$Ph_2P(O)C_6H_4CO_2CH_3$ (δ_{Me} 3.41) and *t*-$BuCO_2CH_3$ (δ_{Me} 3.59) as well as HacacP. By comparison with the mesitylene methyl resonance, it was established that it was almost equimolar with the two esters. These results were corroborated by GLC analysis for *t*-$BuCO_2CH_3$ on an OV-225 column. The *o*-$Ph_2P(O)C_6H_4CO_2H$ formed prior to esterification was also quantified by ^{31}P NMR spectroscopy using Ph_3PS as an internal standard.

Oxygen Uptake by $Cu_2(acacP)_2$. The pressure of a thermostated (47 °C) cell containing **1** (10 mg, 0.011 mmol) and 2.5 mL of *o*-dichlorobenzene was monitored by a Baratron pressure gauge for 24 h. After 22 h, the pressure had leveled off at a pressure drop of 29 torr; i.e. 1.2 equiv of O_2 was taken up by **1**. Analysis of the head gas by GLC on a 3-ft Spherocarb column revealed that 0.05 equiv of CO_2 was produced per equiv of **1**.

Hydrolysis Reaction of $Cu(acacP(O))_2$. $Cu(acacP(O))_2$ was prepared by treatment of $Cu(OAc)_2{\cdot}H_2O$ (49.4 mg, 0.25 mmol) with HacacP(O) (200 mg, 0.5 mmol) in warm methanol. The blue-green copper derivative was purified by chromatography of a CH_2Cl_2 solution on a 3 × 48 cm S-X4 Biobeads column. A CH_2Cl_2 solution (50 mL) of this blue-green copper product and water (1 mL) was charged into a pressure bottle at 40 psig of O_2 (room temperature). This reaction vessel was heated at 90–100 °C for 24 h. A small amount of decomposition was observed as brown solid. The blue-green solution was treated with methanethiol, the precipitated $[Cu(SCH_3)]_n$ was removed by filtration through Celite, and the solvent was removed in vacuo from the yellow solution. Its $^{31}P\{^1H\}$ NMR spectrum (acetone-d_6) consisted of one resonance at δ 26.2 assigned to HacacP(O).

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Table I. Crystal Data, Details of Data Collection, Structure Solution, and Refinement

	2	**3**
a, Å	13.592 (4)	9.750 (2)
b, Å	14.913 (5)	16.399 (3)
c, Å	18.501 (5)	16.698 (4)
α, deg	85.78 (3)	
β, deg	86.19 (2)	97.25 (2)
γ, deg	72.61 (2)	
V, Å^3	3565.2 (19)	2648.5 (10)
space group	$P\bar{1}$ [No. 2, C_i^1]	$P2_1/n$ [No. 14, C_{2h}^5]
Z	2	2
d(calcd), g cm^{-1}	1.138	1.328
diffractometer	Nicolet R3	
radiation	Mo Kα (graphite monochromator)	
scan	ω	$2\theta/\theta$
μ, cm^{-1}	7.17	9.17
temp, °C	24	24
cryst dimens, mm; color	0.22 × 0.30 × 0.41; green	0.35 × 0.35 × 0.35; blue
scan speed, deg/min	3.0	5.0
scan range, deg	$3.0 \leqslant 2\theta \leqslant 45.0$	$3.0 \leqslant 2\theta \leqslant 45.0$
data collcd	$\pm h, \pm k, +l$	$\pm h, +k, +l$
no. of unique data	8638 (9157 collcd)	3407 (3876 collcd)
no. of unique data with $I \geqslant n\sigma(I)$	6296 ($n = 3$)	2304 ($n = 2$)
R_F, %	9.79	10.5
R_{wF}, %	9.44	10.2
GOF	2.23	1.21
final diff map		
highest peak, e/Å^3	1.44	0.67
lowest peak, e/Å^3	−0.46	−0.65

$Cu_2(acacP)_2(\mu\text{-}O_2CC_6H_4P(O)Ph_2)$ (2) from $Cu(O_2CC_6H_4P(O)Ph_2)_2$. To a CH_2Cl_2 solution (50 mL) of **1** (50 mg, 0.056 mmol) and HacacP (40 mg, 0.111 mmol) was added $Cu(O_2CC_6H_4P(O)Ph_2)_2$ (78.3 mg, 0.111 mmol). After addition of methanol (20 mL), green crystals were deposited that were recrystallized from methanol to give 44% yield (51 mg). Anal. Calcd for $C_{69}H_{62}Cu_2O_7P_2$: C, 67.75; H, 5.07. Found: C, 68.19; H, 4.93. A similar preparation of $Cu_2(acacP)_2(\mu\text{-}O_2CPh)$ from $Cu_2(acacP)_2$, $Cu(O_2CPh)_2$, and HacacP gave $Cu_2(acacP)_2(\mu\text{-}O_2CPh)$ in 72% yield.

X-ray Crystallography. Considerable difficulty was experienced in mounting a crystal of $Cu_2(acacP)_2(Ph_2P(O)C_6H_4CO_2)$ (**2**) suitable for diffraction studies. On exposure to an atmosphere not saturated with MeOH, crystals desolvated within a few seconds, leaving powdery residues. Mounting specimens in capillary tubes with mother liquor also proved unsatisfactory; due to the high solubility of **2** in MeOH slight temperature flucuations led to solution/dissolution of the specimen and movement of the crystal in the capillary tube. The mounting problem was solved by transferring the crystal with mother liquor to a spot plate containing a drop of quick-setting epoxy resin; the crystal was pushed from the mother liquor into the resin that was then allowed to become semirigid. Excess resin was trimmed from the specimen to afford an encapsulated crystal, and additional resin was used to affix the crystal to a fine glass fiber. The crystal selected for data collection was the best of the 21 screened, but was still of low quality (large mosaic spread).

The unit-cell parameters were obtained from a least-squares fit of the angular settings of 25 well-centered reflections ($20° \leq 2\theta \leq 30°$). The triclinic space group $P\bar{1}$ was confirmed by the satisfactory solution and refinement of the structure; no lattice of higher symmetry could be found. The equality of the bond lengths and the planarity of the phenyl rings suggested that the cell is correctly described as triclinic. The details of the data collection and results of refinement are summarized in Table I.

Lp and empirical (ψ scan) absorption corrections were used, but none for decay was required. The structure was solved by using the direct methods routine RANT,[14] involving tangent refinement of random starting phases. (All other direct methods routines attempted failed to solve the structure.) The E-map with the best combined figures of merit contained the positions of the two Cu and the three P atoms, and nine subsequent difference Fourier syntheses revealed the locations of the 85 remaining non-hydrogen atoms. The final refinement cycles, by blocked cascade methods, used anisotropic temperature factors for all non-hydrogen atoms, except for the 36 carbon atoms in the six nonbridging phenyl groups, and hydrogen atoms as fixed, idealized, and updated contributions. Fragments of four disordered and scattered molecules of MeOH were also included in the final refinement (the CMX and OMX atoms) as refined, isotropic contributions. The highest peaks on the final difference map revealed that additional fractional occupancy (SOF ≅ 0.35) locations for the solvent molecules existed, but their inclusion in further refinement was deemed unlikely to provide a significant improvement in the quality of the structure of the Cu complex and was, therefore, not attempted. In all, 513 parameters were refined from 6296 reflections ($I \geq 3\sigma(I)$). The results of refinement are provided in Table I.

Table II. Selected Bond Distances and Angles in $Cu_2(acacP)_2(Ph_2P(O)C_6H_4CO_2)$ (**2**)[a]

Distances, Å			
Cu(1)···Cu(2)	3.269 (1)	O(1)–C(3)	1.23 (1)
Cu(1)–O(1)	1.925 (7)	C(3)–C(2)	1.41 (1)
Cu(1)–O(2)	1.961 (7)	C(2)–C(1)	1.33 (1)
Cu(1)–O(3)	1.897 (7)	C(1)–O(2)	1.30 (1)
Cu(1)–O(4)	1.933 (6)	O(3)–C(7)	1.28 (1)
Cu(1)–O(5)	2.358 (7)	C(7)–C(6)	1.36 (1)
Cu(2)–O(5)	2.102 (6)	C(6)–C(5)	1.38 (1)
Cu(2)–P(1)	2.229 (3)	C(5)–O(4)	1.27 (1)
Cu(2)–P(2)	2.233 (3)	O(5)–C(9)	1.27 (1)
P(3)–O(7)	1.509 (8)	C(9)–O(6)	1.24 (1)

Angles, deg			
Cu(1)–O(5)–Cu(2)	94.1 (2)	O(3)–Cu(1)–O(4)	94.0 (3)
O(1)–Cu(1)–O(2)	91.5 (3)	O(3)–Cu(1)–O(5)	99.0 (3)
O(1)–Cu(1)–O(3)	84.0 (3)	O(4)–Cu(1)–O(5)	82.8 (3)
O(1)–Cu(1)–O(4)	175.7 (3)	P(1)–Cu(2)–P(2)	129.8 (1)
O(1)–Cu(1)–O(5)	101.3 (3)	P(1)–Cu(2)–O(5)	124.0 (2)
O(2)–Cu(1)–O(3)	173.8 (3)	P(2)–Cu(2)–O(5)	105.9 (2)
O(2)–Cu(1)–O(4)	90.2 (3)	Cu(1)–O(5)–C(9)	149.2 (7)
O(2)–Cu(1)–O(5)	86.0 (3)	Cu(2)–O(5)–C(9)	99.8 (6)

[a] Atoms are labeled in agreement with Figure 3.

A review of trends of Miller index, parity group, and (sin θ)/λ revealed no systematic trends in the data. Table II provides selected bond distances and angles for **2**.

Blue crystals of $[Cu(acacP(O))(OCH_3)]_2{\cdot}2CH_3OH$ (**3**) were mounted on a glass fiber and coated with epoxy resin. Crystal data are given in Table I. Preliminary photographic work indicated that the crystals were of only fair crystallographic quality and showed a low diffraction intensity and a broad mosaic spread. Severe radiation-induced crystal decay was experienced during data collectiopn (40% decay after 24-h irradiation at 1500-W tube power). Data from four crystals were used to obtain the final data set; check reflection intensities were used to provide interlayer scale factors. No attempt was made to correct the data for absorption effects, but the data for each crystal were corrected for decay.

The structure was solved by the direct methods routine SOLV, which yielded the positions of the Cu and P atoms; subsequent difference Fourier syntheses yielded the locations of the remaining non-hydrogen atoms. The molecule resides on a crystallographic center of symmetry located at the midpoint of the Cu···Cu′ vector. Least-squares refinement of a model containing all non-hydrogen atoms with anisotropic thermal parameters and hydrogen atoms positioned in fixed, idealized locations converged at $R_f = 0.1054$, $R_{wF} = 0.0995$, and GOF = 1.183. The rather high residuals are likely the result of a combination of effects: low crystal quality, extensive decay, merging of four data sets, and the absence of a correction for absorption.

The final difference map showed only a diffuse and chemically meaningless background (max = 0.67 e Å^{-3}). No unusual trends with regard to parity group, sin θ, on Miller index were evident in the data. The results of refinement are provided in Table I. Selected bond distances and angles for **3** are collected in Table III.

Complete listings of all atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and structure factors for both **2** and **3** are available as supplementary material.

Results

Ligand Synthesis. The complete details for the synthesis of the chelating agent, (*o*-(diphenylphosphino)benzoyl)pina-

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(14) This and all other computer programs are contained in the SHELXTL (version 3.0) program package written by G. Sheldrick and distributed by the Nicolet Corp.

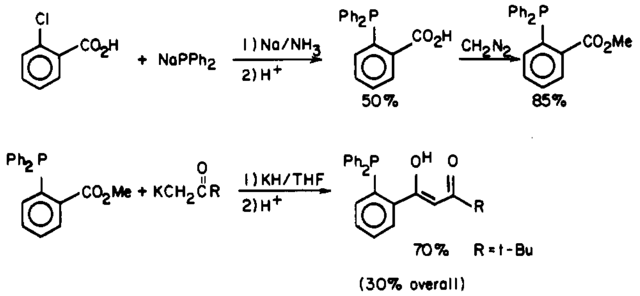
Table III. Selected Bond Distances and Angles for $[Cu(acacP(O))(OCH_3)]_2\cdot 2CH_3OH$ (3)[a]

Distances, Å			
Cu···Cu'	2.982 (3)	P-O(3)	1.502 (9)
Cu-O(1)	1.936 (9)	O(1)-C(1)	1.259 (14)
Cu-O(2)	1.939 (8)	C(1)-C(2)	1.434 (18)
Cu-OT	2.418 (10)	O(2)-C(3)	1.269 (13)
Cu-OB	1.925 (9)	OB-CB	1.360 (17)
Cu-OB'	1.922 (9)	OT-CT	1.359 (23)

Angles, deg			
Cu-OB-Cu'	101.6 (4)	OT-Cu-O(2)	85.6 (4)
O(1)-Cu-O(2)	94.2 (3)	OT-Cu-OB'	99.1 (4)
OB-Cu-O(2)	94.2 (4)	OB-Cu-OB'	78.4 (4)
OB-Cu-O(1)	161.2 (4)	Cu-OT-CT	130.3 (10)
OT-Cu-O(1)	94.4 (4)	Cu-OB-CB	126.2 (8)

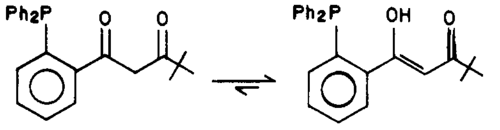
[a] Atoms are labeled in agreement with Figure 2. Primes denote inversion-related atoms.

Scheme I



colone (HacacP), are reported here. This preparation (Scheme I) consists of three steps beginning with conversion of the inexpensive o-chlorobenzoic acid to o-(diphenylphosphino)benzoic acid according to the methods of Mason.[13,15] Following esterification using diazomethane, the final step involves the Claisen condensation of the methyl ester with the potassium enolate of pinacolone. This ligand is easily obtained as air-stable, pale yellow crystals from hot methanol. In this way one can routinely obtain HacacP in overall yields of 29%.

The phosphine β-diketone ligand primarily exists in the enol form in $CDCl_3$ solution (eq 1) as established by the ^1H NMR



(1)

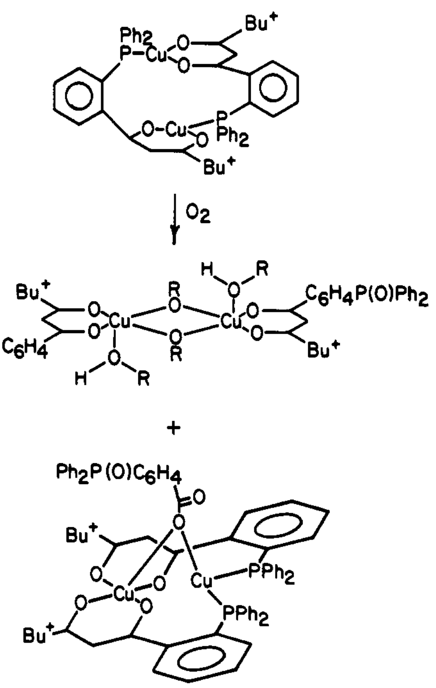
spectrum, which shows resonances of relative intensity of one hydrogen at 5.87 ppm assignable to the methine proton and at 14.8 ppm that is readily exchangeable with D_2O. No resonance attributable to a methylene is observed. Additionally, the infrared spectrum of a mineral oil mull of HacacP reveals strong absorptions at 1605 and 1582 cm^{-1} that may be compared with those at 1608 and 1571 cm^{-1} found for the enol form of benzoylacetone. Acetylacetone in the diketone form exhibits an IR absorption at 1709 cm^{-1}.[16]

Synthesis of $M_2(acacP)_2$ Complexes. Upon addition of triethylamine to an acetonitrile solution of $[Cu(MeCN)_4]ClO_4$ and HacacP, yellow microcrystalline $Cu_2(acacP)_2$ (**1**) is deposited in good yield (eq 2). The analogous cream-colored

$$[Cu(MeCN)_4]ClO_4 + HacacP + NEt_3 \rightarrow {}^1/_2Cu_2(acacP)_2 + HNEt_3ClO_4 + 4MeCN \quad (2)$$

silver complex $Ag_2(acacP)_2$ was synthesized under similar conditions from $AgClO_4$. Both of these species were characterized by combustion analysis, IR, ^1H NMR and ^{31}P NMR spectroscopy, and field desorption mass spectrometry (FDMS). The formulation of these complexes as binuclear species is supported by the observation of molecular ions (M^+) in the FDMS of both the copper and silver complexes. The IR spectra of these complexes reveal carbonyl absorptions at 1575–1595 cm^{-1}, ca. 10–30 cm^{-1} lower frequency than the free ligand. Similar frequency shifts have been noted for other β-diketones.[17] The coordination of the ligand to the metal centers is also reflected in the ^1H NMR spectra by disappearance of the hydroxy resonance and shift of both the methine and *tert*-butyl signals to higher field. Phosphine coordination is indicated by the downfield shift of the phosphine resonances in the ^{31}P NMR spectra at −3.6 and +8.4 ppm, for the copper and silver complexes, respectively, as compared to the free ligand at −9.0 ppm.

Scheme II



On the basis of similarities of our HacacP ligand to other compartmentalized ligand systems,[18] it seemed likely that the metals would be pseudotetrahedrally coordinated. The ^{31}P NMR spectrum of complex $Ag_2(acacP)_2$ is characterized by a $^1J(^{107}Ag,^{31}P)$ of 718 Hz, which is large in comparison with $^1J(^{107}Ag,^{31}P)$ of 320 Hz normally associated with tetrahedrally coordinated silver.[19] This led us to conclude that the coordination number for these complexes would be less than 4. In order to clarify the matter, we characterized **1** by single-crystal X-ray diffraction.

The structure of **1** was described in an earlier paper.[5] Its molecular structure consists of two trigonally coordinated copper(I) units related through an inversion center and bridged by the phenylene fragment of the acacP ligand (Figure 1). The coordination sphere of the copper center is very nearly planar, with the metal atom within 0.0087 (5) Å of the plane containing the PO_2 donor set. The cofacially positioned coordinatively unsaturated copper(I) centers are well separated from

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(16) Rasmussen, R. S.; Tunnicliff, D. D.; Brattain, R. R. *J. Am. Chem. Soc.* **1949**, *71*, 1068.

(17) Holtzclaw, H. F.; Collman, J. P. *J. Am. Chem. Soc.* **1957**, *79*, 3319.

(18) (a) Lintvedt, R. L.; Tomlonovic, B.; Fenton, D. E.; Glick, M. D. *Adv. Chem. Ser.* **1976**, *No. 150*, 407. (b) Casellato, U.; Vigato, P. A.; Fenton, D. E.; Vidali, M. *Chem. Soc. Rev.* **1979**, *8*, 199.

(19) (a) Pregosin, P. L.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Diehl, P., Flock, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1979; Vol. 16. (b) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386.

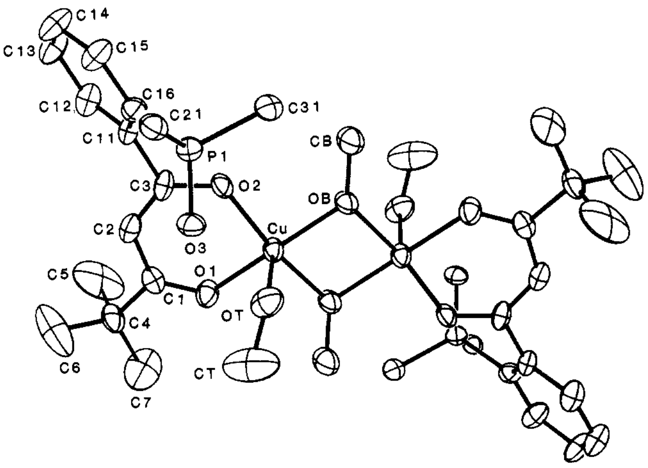

Figure 2. ORTEP plot of the non-hydrogen atoms of the $Cu_2(acacP(O))_2(OCH_3)_2$ molecule (**3**) with thermal ellipsoids set at 40% probability level. For clarity, the monosubstituted phenyl groups are omitted except for the ipso carbon atoms.

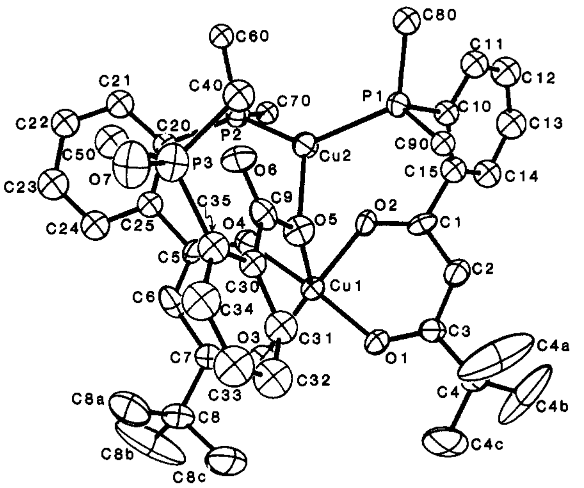

Figure 3. ORTEP plot of the non-hydrogen atoms of the $Cu_2(acacP)_2(o\text{-}Ph_2P(O)C_6H_4CO_2)$ molecule (**2**) with thermal ellipsoids set at 40% probability level. For clarity, the monosubstituted phenyl groups are omitted except for the ipso carbon atoms.

one another by a nonbonding distance of 3.7682 (7) Å. The Cu(2)–P distances of ~2.23 Å and P(1)–Cu(2)–P(2) of 129.8° compare favorably with that of $Cu(CF_3C(O)CHC(O)CF_3)(PPh_3)_2$[20] (2.25 Å and 127°).

The Oxygenation of 1. $Cu_2(acacP)_2$ (**1**) is air-stable in the solid state, but its solutions assume a green color in air. The nature of this oxidation was studied by examining the products obtained when a CH_2Cl_2 solution of **1** was allowed to react under an atmosphere of molecular oxygen. Purification of the reaction mixture using gel permeation chromatography afforded two products, one of which was isolated in crystalline form and identified as $Cu_2(acacP)_2(\mu\text{-}Ph_2P(O)C_6H_4CO_2)$ (**2**), based on a single-crystal X-ray diffraction study (Scheme II). The osmometric molecular weight supports this formulation of the copper complex as does the observation of a ν_{PO} band at 1168 cm^{-1} in its IR spectrum. The EPR spectrum of a toluene/CH_2Cl_2 glass ($g_\parallel = 2.29$, $g_\perp = 2.07$; $A_\parallel = 494$ MHz, $A_\perp = 40$ MHz) is very similar to those of other copper β-diketonate complexes (e.g., $Cu(PhCOCHCOMe)_2$ in $CHCl_3$ glass shows $g_\parallel = 2.26$, $g_\perp = 2.05$, $A_\parallel = 546$ MHz, and $A_\perp = 63$ MHz),[21] indicating approximately axial symmetry about the copper(II) center.

In the course of isolating pure samples of **2** by fractional crystallization, we also obtained crystals of $[Cu(acacP(O))(OCH_3)]_2{\cdot}2CH_3OH$ (**3**), which was also characterized by single-crystal X-ray diffraction as having the structure shown in Figure 2. This dimeric copper(II) complex is similar structurally (Table III) to less ornate derivatives like $[Cu(acac)(OCH_2Ph)]_2$,[22] although in **3** methanol functions as an axial base. The important feature of the structure of **3** is that it indicates a second "simpler" oxidation process that competes with the formation of **2**. We assume that the methoxy bridges arise from transesterification during workup. The oxygen stoichiometry required for the formation of **3** from **1** is $^3/_2$ O_2/equiv of **1** (eq 3 and 4).

$$Cu_2(acacP)_2 + {}^3/_2O_2 + H_2O \rightarrow Cu_2(acacP(O))_2(OH)_2 \quad (3)$$

$$Cu_2(acacP(O))_2(OH)_2 + 2MeOH \rightarrow Cu_2(acacP(O))_2(OMe)_2 + 2H_2O \quad (4)$$

Subsequent to a typical oxygenation reaction, the green homogeneous solution could be quantitatively demetalated with methanethiol concomitant with the precipitation of yellow, polymeric $[Cu(SCH_3)]_n$.[23] This reaction is presumed to occur according to eq 5 or 6, depending on the oxidation state of the

$$CuX_2 + 2CH_3SH \rightarrow (1/n)[Cu(SCH_3)]_n + 2HX + {}^1/_2(CH_3S)_2 \quad (5)$$

$$CuX + CH_3SH \rightarrow (1/n)[Cu(SCH_3)]_n + HX \quad (6)$$

copper complexes involved. The experimental advantage to this procedure is that anionic ligands are obtained in their neutral protonated forms and the organosulfur byproducts are volatile. Subsequent to removal of the copper mercaptide polymer, the organic products were treated with an excess of diazomethane to convert any carboxylic acids to their respective esters. The resulting products were analyzed by three methods. ^{31}P NMR spectroscopy established that ~12% of the acacP had been converted to $o\text{-}Ph_2P(O)C_6H_4CO_2H$. This particular carboxylic acid is a known compound as is its copper(II) derivative.[12] The remaining phosphorus-containing products were HacacP and HacacP(O) although the relative amounts of these compounds were not determined. Gas chromatography revealed methylpivalate, $(CH_3)_3CCO_2CH_3$, as the only volatile esterification product. The yield of this species was 10%, based on the total acacP, comparable to that observed for $o\text{-}Ph_2P(O)C_6H_4CO_2H$. Lastly, ^1H NMR spectroscopy was used to establish the relative quantities of the two methyl esters by integration of their well-separated methyl resonances: The $o\text{-}Ph_2P(O)C_6H_4CO_2CH_3$ to $(CH_3)_3CCO_2CH_3$ ratio was close to 1:1, and the yields were 12.5%. The low yields of carboxylic acids clearly indicate that whatever the mechanism of oxidative C–C cleavage is, it is less facile than the more obvious reaction that involves "simple" oxidations of copper(I) to copper(II) and phosphorus(III) to phosphorus(V).

Further information bearing on the oxygenation of **1** was obtained by an O_2-uptake measurement and an analysis of the gaseous products. At 50 °C in *o*-dichlorobenzene, the O_2 consumption leveled off at 1.2 equiv of O_2/equiv of **1**. Chromatographic analysis of the head gas revealed the evolution of 0.04 equiv of CO_2/equiv of **1** while no CO was detected.

Description of the Structure of 2. The molecular structure of $Cu_2(acacP)_2(\mu\text{-}o\text{-}Ph_2P(O)C_6H_4CO_2)$ was determined by

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[20] Bartlett, M.; Palenik, G. J. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1969**, *25*, S173.

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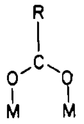
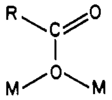
[22] Andrew, J. E.; Blake, A. B. *J. Chem. Soc., Dalton Trans.* **1973**, 1102.

[23] Reid, E. E. "The Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co., Inc.: New York, 1958; Vol. 1, Chapter 2.

single-crystal X-ray diffraction and is depicted in Figure 3. Relevant bond distances and angles are collected in Table II. Its molecular structure consists of a trigonally planar copper(I) linked to a square-pyramidal copper(II) by two acacP ligands although coordination of the enolate oxygen of cupric β-diketonate to the 16e copper(I) center would be expected in a manner analogous to the structure of $Cu_2(acacP)_2(\mu\text{-}O_2CC_6H_4OCH_3)$.[6] An unusual structural feature is the manner in which the carboxylate bridges the two metals via one oxygen atom, reminiscent of the structure of polymeric cuprous acetate[24] or polymeric copper(II) bis(propionato)-*p*-toluidine,[25] instead of via two oxygens as is commonly observed for other copper dimers, i.e. $Cu_2(O_2CR)_4$[26] and $Cu_2(acacP)_2(\mu\text{-}m\text{-}CH_3OC_6H_4CO_2)$.[6]





The finding that $o\text{-}Ph_2P(O)C_6H_4CO_2^-$ adopts this unique bridging mode is most likely due to the steric bulk of the $o\text{-}Ph_2P(O)$ substituent that blocks access of the second carboxylate oxygen to the copper.

Supplementary Synthetic Studies. The recurring presence of the mixed-valent Cu(I)–Cu(II) species suggests that it is an intrinsically stable species and it should be possible to prepare it from simpler, labile precursors. This was found to be the case; employing the reactions shown in eq 7 and 8, we prepared the desired products in high yields.

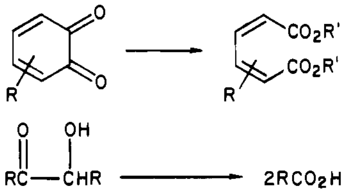
$$2Cu(O_2CPh)_2 + Cu_2(acacP)_2 + 2HacacP \rightarrow 2Cu_2(acacP)_2(O_2CPh) + 2PhCO_2H \quad (7)$$

$$2Cu(O_2CC_6H_4P(O)Ph_2)_2 + Cu_2(acacP)_2 + 2HacacP \rightarrow 2Cu_2(acacP)_2(O_2CC_6H_4P(O)Ph_2) + 2Ph_2P(O)C_6H_4CO_2H \quad (8)$$

It is conceivable that the β-diketone could be cleaved by trace amounts of water as Fackler[27] has observed in the hydrolysis of $Cu(CF_3C(O)CHC(O)CF_3)_2$ in pyridine to give $Cu(py)_4(O_2CCF_3)_2$. To verify that this does not occur in our system, a CH_2Cl_2 solution of $Cu(acacPO)_2$ and H_2O under an oxygen atmosphere was heated at 90 °C for 24 h. The only phosphorus-containing product was HacacP(O) as identified by ^{31}P NMR analysis of the demetalated reaction mixture.

Discussion

The transformation of **1** to **2** involves both ligand- and metal-centered oxidations. Other examples of copper-induced ligand oxidation are known. For example copper–O_2 systems are capable of the oxidative cleavage of quinones[10,28] and α-hydroxy ketones.[29]



Furthermore, recent work has established the ability of copper(I)–O_2 systems for arene hydroxylation.[9,10] In view of the complexity of $Cu_2(acacP)_2$–O_2 reaction, it is impossible to draw firm mechanistic conclusions from the present results. The modest yields of **2** realized in the oxygenation of **1** can be explained by the competing oxidation of **1** to $Cu_2(acacP(O))_2(OH)_2$. Since such a process is to be expected on the basis of the known chemistry of Cu(I) and tertiary phosphines,[30] the fact that C–C bond scission competes at all is somewhat surprising.

The observation that **2** is a mixed-valent Cu(II)–Cu(I) species cannot be construed to be of any mechanistic significance in view of the kinetic lability of these metal complexes and the stability of the mixed-valent complex. It is important to recognize that the structure of **2** protects this complex from further oxidation by stabilizing the copper(I) by coordination to *two* phosphine moieties. Whereas in **1** each Cu(I) is coordinated to only one phosphine and two hard oxygen donors, the same donors are redistributed in 2 so as to provide the hard and soft copper centers with its preferred array of donor atoms. Completely consistent with this rationale is the observation that $Cu_2(acacP)_2$ only undergoes 1e oxidative addition by excess dibenzoyl peroxide, yielding $Cu(\mu\text{-}O_2CPh)Cu(acacP)_2$, which is quite similar structurally[6] to **2**.

Acknowledgment. The purchase of the X-ray diffractometer was supported by a grant from the NSF to University of Delaware. The work at University of Illinois was supported in part by Dow Chemical Co. T.B.R. is a fellow of the A. P. Sloan and Camille and Henry Dreyfus Foundations. We would like to thank Professor Kenneth Suslick for helpful discussions and the loan of equipment for the oxygen-uptake experiment.

Registry No. **1**, 79931-93-4; **2**, 91443-73-1; **3**, 91443-78-6; HacacP, 91443-74-2; $Ag_2(acacP)_2$, 79931-92-3; $Cu(acacP(O))_2$, 91443-75-3; $Cu_2(acacP)_2(\mu\text{-}O_2CPh)$, 91443-77-5; $[Cu(MeCN)_4]ClO_4$, 14057-91-1; $Cu(O_2CC_6H_4P(O)Ph_2)_2$, 91443-76-4; $o\text{-}Ph_2PC_6H_4CO_2CH_3$, 79932-99-3; $o\text{-}Ph_2PC_6H_4CO_2H$, 17261-28-8; pinacolone, 75-97-8.

Supplementary Material Available: Tables of atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates and temperature factors, and structure factors (72 pages). Ordering information is given on any current masthead page.

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(27) Pradilla, S. J.; Chen, H. W.; Koknat, F. W.; Fackler, J. P., Jr. *Inorg. Chem.* **1979**, *18*, 3519.

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