

tentative conclusion concerning the impact of electrophilic catalyst on the mode of reaction in these and related cyclohexane ring forming substrates is that electrophilic catalysts which effect considerable cationic charge development with limited counterion donation to the trimethylstannyl moiety promote β -hydride transfer (BF_3 , $\text{CF}_3\text{CO}_2\text{H}$, $\text{Me}_3\text{Si-OSO}_2\text{CF}_3$), whereas those which effect cationic charge buildup concurrent with anionic ligand donation to the trimethyl stannyl unit promote carbon-carbon bond formation (TiCl_4 , SnCl_4).

Our initial investigations of tin(IV)-mediated internal reaction processes have established that the tetraalkyltin moiety and carbon-centered electrophilic precursor are compatible until electrophilic activation and that an array of carbon-centered electrophiles and carbon-tin nucleophiles can be employed in these reactions, thereby providing variable product functionality. The studies outlined here have helped to define those substrate and reaction condition parameters which direct the mode of carbon-tin bond mediated reaction to carbon-carbon bond formation or β -hydride transfer. In addition, the finding of a Lewis acid dependence on the mode of reactivity in these cyclohexane ring forming substrates could have implications in other Lewis acid catalyzed reaction processes.

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Supplementary Material Available: Spectral and analytical data for new compounds (1 page). Ordering information is given on any current masthead page.

Synthesis and Structure of a "Dicuprophane", a Dicopper(I) Complex Derived from *o*-(Diphenylphosphino)benzoylpinacolone

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We wish to report the preparation of an unusual binucleating chelating agent and the synthesis and structure of its copper(I) complex which contains two cofacial three-coordinate $16e^-$ copper(I) moieties. The present results bear on the general challenge of the preparation of bimetallic coordination compounds containing metal ions in *reactive* oxidation states. Representative developments in this field include studies of bimetallic complexes of 2-(diphenylphosphino)pyridine,¹ bis(diphenylphosphino)methane,² and imine derivatives of 2,6-diformylcresol.³

With the goal of preparing an unsymmetrical uninegative compartmentalized chelating agent capable of binding two metal ions in low oxidation states, we synthesized the phosphine-substituted β -diketone ligand *o*-[(diphenylphosphino)benzoyl]pinacolone.⁴ The target compound was efficiently constructed in three

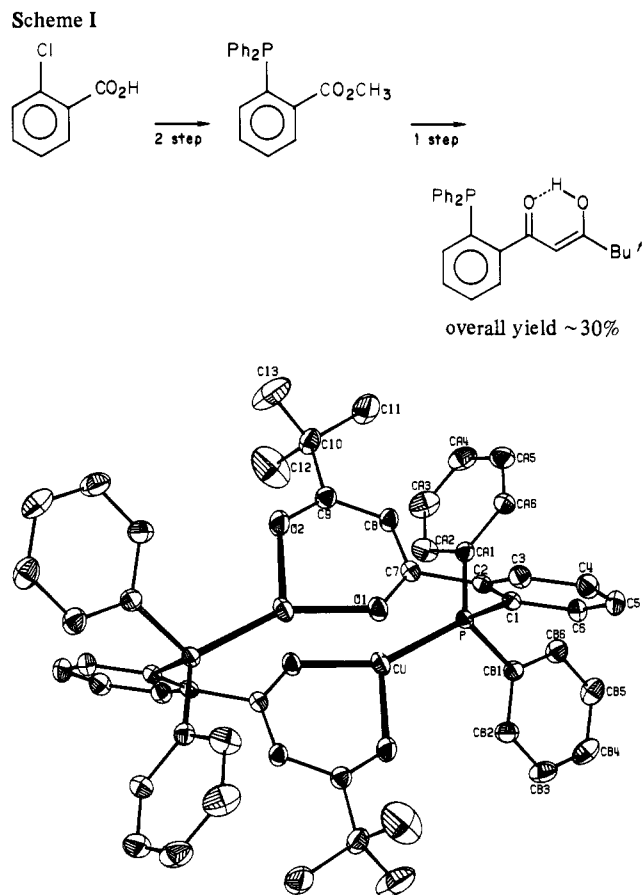


Figure 1. ORTEP plot of the nonhydrogen atoms of the $[\text{Cu}(\text{acacP})]_2$ molecule with thermal ellipsoids set at the 50% probability level.

steps on a 0.06-mol scale by using inexpensive reagents (Scheme I). The product, which we call HacacP, exists in the enol form in CDCl_3 solution and was isolated as pale yellow, air-stable crystals which are readily soluble in polar organic solvents.

Treatment of HacacP with 1 equiv of $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$ in acetonitrile in the presence of triethylamine quantitatively afforded yellow microcrystalline $[\text{Cu}(\text{acacP})]_2$ (**1**) (eq 1) which was

$$2[\text{Cu}(\text{MeCN})_4]\text{ClO}_4 + 2\text{HacacP} + 2\text{Et}_3\text{N} \rightarrow [\text{Cu}(\text{acacP})]_2 + 8\text{MeCN} + 2\text{Et}_3\text{NHCIO}_4 \quad (1)$$

characterized by combustion analysis, IR, ^1H and ^{31}P NMR, and field desorption mass spectrometry.⁷ These measurements all indicated the expected stoichiometry and a symmetrical structure but provided no definitive information concerning the geometry about the metal ions. On the basis of extensive precedent of other structurally characterized dimetal(II) complexes derived from

(4) *o*-(Diphenylphosphino)benzoic acid was prepared from *o*-chlorobenzoic acid and NaPh_2 .⁵ Esterification of the acid with diazomethane gave the methyl ester *o*- $\text{Ph}_2\text{PC}_6\text{H}_4\text{CO}_2\text{CH}_3$ in 85% yield as colorless crystals from methanol, mp 96–97 °C; IR (mull) 1712 cm^{-1} (s); ^1H NMR (90 MHz, CDCl_3 solution) δ 7.6–6.9 (m, 14 H), 3.70 (s, 3 H); $^{31}\text{P}\{^1\text{H}\}$ NMR (40.5 MHz, CDCl_3 solution) 5.1 ppm upfield of 85% H_3PO_4 . Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{O}_2\text{P}$: C, 75.00; H, 5.35; P, 9.67. Found: C, 75.00; H, 5.32; P, 9.70. Condensation of the methyl ester with $\text{KCH}_2\text{COC}(\text{CH}_3)_3$ in THF followed by acidification (HCl) and crystallization (methanol) gave a 65% yield of cream colored crystals, mp 118 °C; IR (mull) 1605 (s), 1580 (s) cm^{-1} ; ^1H NMR (90 MHz, CDCl_3 solution) δ 14.8 (br s, 1 H), 6.8–7.7 (m, 14 H), 5.87 (s, 1 H), 1.09 (s, 9 H); $^{31}\text{P}\{^1\text{H}\}$ NMR (40.5 MHz, CDCl_3 solution) 8.98 ppm upfield of 85% H_3PO_4 . Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{O}_2\text{P}$: C, 77.32; H, 6.44; P, 7.99. Found: C, 77.22; H, 6.56; P, 8.02.

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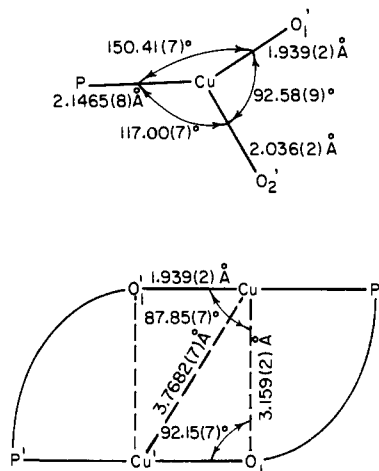


Figure 2. The in-plane and out-of-plane structural parameters for the $[\text{Cu}(\text{acacP})_2]$ molecule; inversion related atoms are indicated by primes.

topologically equivalent ligands,^{8,9} it appeared likely that the copper(I) moieties would be pseudotetrahedral as are most copper(I)-phosphine complexes. On the other hand, the values of $J(^{109}\text{Ag}, ^{31}\text{P})$ and $J(^{107}\text{Ag}, ^{31}\text{P})$ of 826 and 718 Hz measured for $[\text{Ag}(\text{acacP})_2]$ ¹⁰ are unusually large for tetracoordinated silver(I).¹¹ Our X-ray crystallographic study clarified this situation by demonstrating that **1** possesses a very unusual structure.

A 0.20- × 0.35- × 0.35-mm crystal obtained by slow diffusion of methanol into a CH_2Cl_2 solution of **1** with exclusion of air was used for data collection. The space group and cell data are as follows: monoclinic, space group $P2_1/n$ with $a = 9.508(2)$ Å, $b = 14.529(3)$ Å, $c = 16.001(5)$ Å, $\beta = 92.01(2)^\circ$, $V = 2209.2(9)$ Å³, $d(\text{calcd}) = 1.356$ g cm⁻³, $d(\text{found}) = 1.34$ g cm⁻³, and $Z = 2$. Three-dimensional diffraction data (a total of 3657 independent reflections having $2\theta(\text{Cu K}\alpha) \leq 130^\circ$) were collected on a Syntex $P2_1$ autodiffractometer by using graphite-monochromated $\text{Cu K}\alpha$ radiation. The position for the Cu atom was located by a weighted (E*F) Patterson synthesis. Subsequent difference Fourier maps revealed the positions of all remaining atoms, including all hydrogens. Least-squares refinement to convergence using anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms gave $R = 0.0388$ and $R_w = 0.0478$.¹²

The structure of **1** consists of two trigonally coordinated copper(I) units¹³ related through the inversion center and bridged by the phenylene fragment of the acacP chelate (Figure 1). The coordination sphere of the copper atom is very nearly planar with the metal atom within 0.0087 (5) Å of the plane containing the PO_2 donor set. The coordination planes of the dimer are parallel since they are inversion related. As indicated in Figure 2, the two in-plane Cu-O distances differ by ~ 0.1 Å while a third, non-bonding oxygen is a further 1.220 Å distant from the metal center.

The present structure is geometrically related to a growing class of bimetallic complexes characterized by cofacially positioned

coordinatively unsaturated, low-valent metal ions¹⁴ ("di-metallophanes").¹⁵ On the basis of synthetic and structural principles illustrated in this work, a range of new homo- and heterobimetallic complexes can now be anticipated by using chemically and topologically equivalent agents.¹⁶

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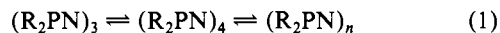
Synthesis of $[(\text{C}_6\text{H}_5\text{NH})\text{PNC}_6\text{H}_5]_3$: A Participant in a Phosphorus(III)-Nitrogen Compound Trimer-Dimer Interconversion Reaction

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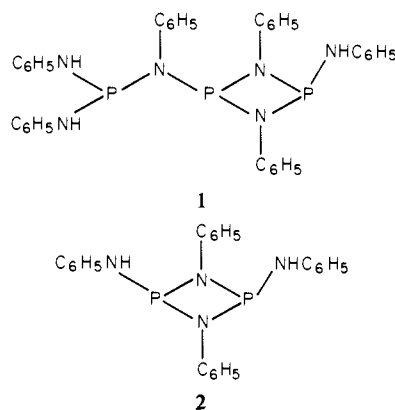
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Oligomer interconversion reactions of phosphorus(V)-nitrogen compounds are well characterized for cyclo- and linear polyphosphazenes, e.g.,^{2,3}



Except for the recently reported dimerization of $[(\text{CH}_3)_3\text{Si}]_2\text{N-PNSi}(\text{CH}_3)_3$,⁴ oligomer interconversions of phosphorus(III)-nitrogen compounds have not been observed. We wish to report now the synthesis and characterization of a novel 1,3,2,4-diazadiphosphetidine $[(\text{C}_6\text{H}_5\text{NH})\text{PNC}_6\text{H}_5]_3$ (**1**) and its conversion to $[(\text{C}_6\text{H}_5\text{NH})\text{PNC}_6\text{H}_5]_2$ (**2**) in what appears to be the first example of a trimer-dimer oligomerization among phosphorus(III)-nitrogen compounds.



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