be expected to behave with respect to their coordinating ability and their structural chemistry in manners similar to the 1,3-di- and 1,3,5-triketones. Therefore, these ligands should provide a convenient entry into an extensive new class of molecular trinuclear complexes, both homo- and heterotrinuclear. This study is the first stage of a long-range project to carefully characterize and investigate the properties of the trinuclear metal complexes of the 1,3,5,7-tetraketonates and their Schiff-base derivatives. A forthcoming paper contains complete structural data for the compound described herein as well as for two other related compounds and the synthesis, magnetic properties, electrochemical results, and spectral properties for several heterotrinuclear 1,3,5,7-tetraketonates.

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Registry No. $[(UO_2)_2(Ni)(DBAA)_2(py)_4]\cdot 2py$, 81205-64-3.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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(8) Blake, A. B.; Fraser, L. R. *J. Chem. Soc., Dalton Trans.* **1974**, 2554.

(9) Fenton, D. E.; Gayda, S. E.; Holmes, P. *Inorg. Chem. Acta* **1977**, *21*, 187.

(10) Guthrie, J. W.; Lintvedt, R. L.; Glick, M. D. *Inorg. Chem.* **1980**, *19*, 2949.

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Synthesis of a Mixed-Valence Copper Complex via Free-Radical Additions to a Copper(I) Dimer

Sir:

We recently described the synthesis and structure of a compound that contains two cofacial, three-coordinate (16e) copper(I) moieties coordinated to two bridging phosphino diketonate compartmentalized ligands.[1] This complex is an unusual example of a readily isolable, coordinatively unsaturated, binuclear copper(I) complex[2] and is ideally suited for oxidative-addition studies. Oxidative additions to bimetallic complexes have received considerable attention recently although the majority of such studies have been restricted to the group 8 metals.[3] The mechanisms for such processes involve either localized (monometallic) or bimetallic substrate binding via formal *two-electron* oxidations of the metal(s) involved. The present report describes the first example of a *one-electron oxidative addition* to a bimetallic complex. The process described herein is particularly novel since it is also characterized by both bimetallic substrate binding and an unprecedented ligand rearrangement.

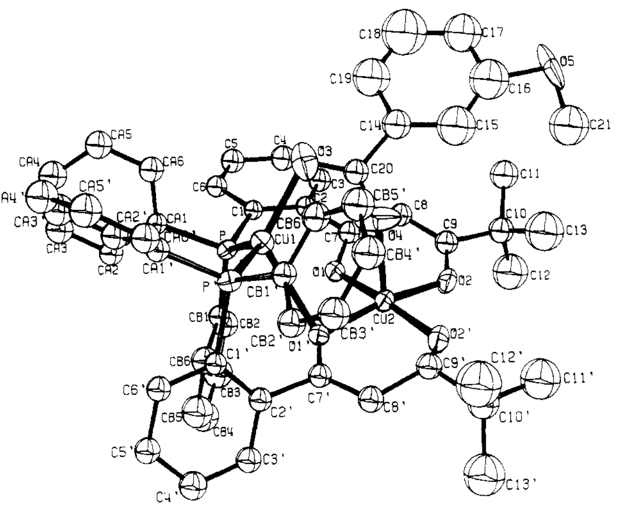

Figure 1. ORTEP plot of the nonhydrogen atoms of the $Cu_2(acacP)_2(3\text{-}CH_3OC_6H_4CO_2)$ molecule with thermal ellipsoids set at the 30% probability level.

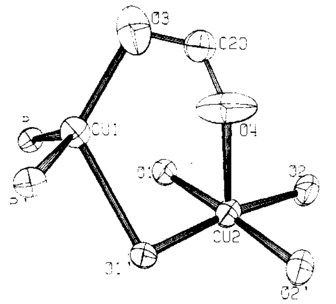

Figure 2. ORTEP plot of the two copper centers with their coordination spheres, including the carboxylate, of the $Cu_2(acacP)_2(3\text{-}CH_3OC_6H_4CO_2)$ molecule with thermal ellipsoids set at the 30% probability level.

Table I. Selected Distances (Å) and Angles (Deg)

Cu1–Cu2	3.321 (2)	Cu2–O2	1.915 (7)
Cu1–P1	2.250 (3)	Cu2–O1′	1.926 (7)
Cu1–P2	2.224 (3)	Cu2–O2′	1.941 (8)
Cu1–O1′	2.524 (7)	Cu2–O4	2.249 (9)
Cu1–O3	2.11 (1)	C20–O3	1.21 (2)
Cu2–O1	1.965 (7)	C20–O4	1.23 (2)
P–Cu1–P′	129.9 (1)	O1–Cu2–O2	91.4 (3)
P–Cu1–O1′	97.4 (2)	O1–Cu2–O1′	88.3 (3)
P–Cu1–O3	104.7 (3)	O1–Cu2–O2′	173.3 (3)
P′–Cu1–O1′	81.4 (2)	O1–Cu2–O4	92.2 (3)
P′–Cu1–O3	119.3 (3)	O2–Cu2–O1′	169.2 (3)
O1′–Cu1–O3	119.8 (3)	O2–Cu2–O2′	86.4 (3)
Cu1–O1′–Cu2	95.6 (3)	O2–Cu2–O4	98.6 (4)
Cu1–O3–C20	107.1 (9)	O1–Cu2–O2′	92.7 (3)
Cu2–O4–C20	133.2 (9)	O1′–Cu2–O4	92.3 (3)
O3–C20–O4	125 (1)	O2′–Cu2–O4	94.3 (4)

Treatment of yellow dichloromethane solutions of the binuclear copper(I) complex of [*o*-(diphenylphosphino)benzoyl]pinacolonate, $[Cu(acacP)]_2$ (**1**), with 1 equiv *or more* of dibenzoyl peroxide results in a rapid color change to green. The lustrous, kelly green crystalline product was obtained in 86% yield by the addition of methanol. While **1** is quite air sensitive in solution, the new complex can be dissolved in polar organic solvents to give aerobically and chromatographically stable solutions. Microanalytical data, osmometry, and

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(1) Rauchfuss, T. B.; Wilson, S. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 6769.

(2) Bulkowski, J. E.; Burk, P. L.; Ludmann, M. F.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498. Gagné, R. R.; Kreh, R. P.; Dodge, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6917. Nelson, S. M.; Esho, F. S.; Drew, M. G. B. *J. Chem. Soc., Chem. Commun.* **1981**, 388. Birker, P. J. M. W. L.; Hendricks, H. M. J.; Reedijk, J. *Inorg. Chim. Acta* **1981**, *55*, L17. Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1868.

(3) For leading references see: Lindsay, C. H.; Benner, L. S.; Balch, A. L. *Inorg. Chem.* **1980**, *19*, 3503. Tolman, C. A.; Meakin, P. Z.; Lindner, D. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 2762. Bonnet, J.-J.; Kalck, P.; Poilblanc, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 551.

(4) All new compounds described herein were analyzed satisfactorily for C, H, Cu, and P (e.g., ref 5).

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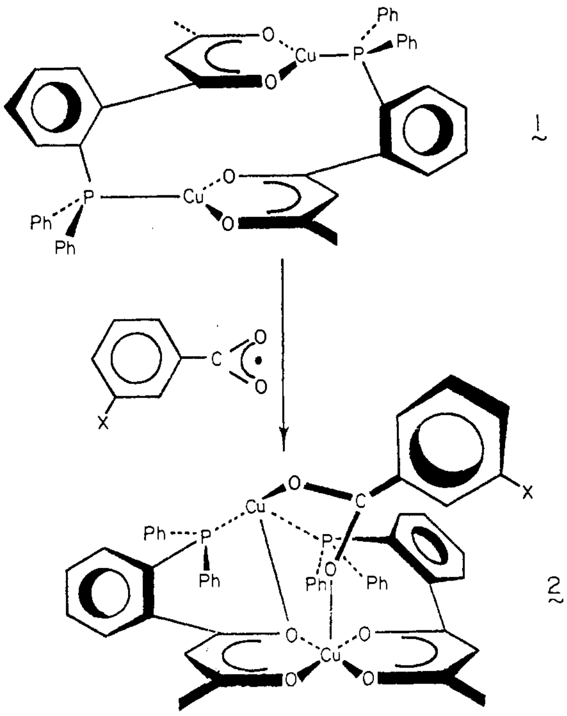
Scheme I



magnetic susceptibility indicated the formula $[Cu_2(acacP)_2(PhCO_2)]$ (**2**).[4,5] The analogous 3-chlorobenzoate derivative $[Cu_2(acacP)_2(3\text{-}ClC_6H_4CO_2)]$[4] was readily prepared from the reaction of **1** with 1 equiv *or more* of 3-chloroperoxybenzoic acid.

Interconversion reactions establish the redox relationship between **1** and **2**. Treatment of **2** with HCl liberates benzoic acid and CuCl(HacacP) (**3**)[4] and induces oxidation of some HacacP to its oxide. Complex **3**, which can also be prepared directly from $CuCl_2$ and HacacP, reacts with base to re-form **1**, thereby completing the cycle (eq 1–3).

$$2Cu_2(acacP)_2O_2CPh + 4HCl + H_2O \rightarrow 3CuCl(HacacP) + 2PhCO_2H + CuCl + HacacPO \tag{1}$$

$$2CuCl(HacacP) + 2NaOCH_3 \rightarrow [Cu(acacP)]_2 + 2NaCl + 2CH_3OH \tag{2}$$

$$[Cu(acacP)]_2 + {}^1/_2(PhCO_2)_2 \rightarrow [Cu_2(acacP)_2O_2CPh] \tag{3}$$

Two interesting questions concern the structure of the mixed-valence copper carboxylates, e.g., **2**. First, copper(II) derivatives of tertiary phosphines are extremely unusual as cupric ions are well-known for their ability to oxidize phosphorus(III) with concomitant formation of copper(I).[6] An additional question of more general import concerned the stoichiometry of the oxidation (eq 3): only one-electron oxidative-addition products formed in reactions involving an excess of very strong oxidizing agents with a potential two-electron reductant (**1**). Both issues were resolved by a single-crystal X-ray diffraction study, a preliminary report of which is described below.

A 0.15 × 0.32 × 0.40 mm crystal of the 3-methoxybenzoate derivative $Cu_2(acacP)_2(3\text{-}CH_3OC_6H_4CO_2)$[7] obtained from CH_2Cl_2–CH_3OH solutions was used for data collection.[8] The locations of the two copper atoms were derived from a Patterson map; subsequent difference Fourier synthesis revealed the positions of the remaining nonhydrogen atoms. All carbon atoms were refined with isotropic thermal parameters, with phenyl rings refined as "ideal" groups.[9] Least-squares refinement to convergence using anisotropic thermal parameters for the remaining nonhydrogen atoms gave an $R = 0.0847$ and $R_w = 0.1138$.[10] All atoms within the coordination sphere of both copper atoms, including the carboxylate portion of the benzoate, were well-defined.

The molecule is depicted in Figure 1 while the coordination spheres of the two metals are shown in Figure 2. Relevant structural parameters are collected in Table I. The molecular structure of **1** consists of tetrahedral copper(I) linked to square-pyramidal copper(II) by two acacP ligands. The copper(II) moiety resides in the "hard" bis(β-diketonate) site while the copper(I) moiety is accommodated by the two phosphines and a bridging enolate oxygen; the oxidatively added substrate bridges the two metals, formally functioning as both an anionic ligand for the copper(I) center and an axial base for the copper(II) center. One acacP ligand remains tridentate following the rearrangement while the other assumes the role of a tetradentate binucleating ligand comparable to the 1,3,5-triketonate-type ligands, whose complexes have been structurally characterized by Glick and co-workers.[11]

While the structure of the mixed-valence complex **2** is novel in its own right, its formation from the symmetrical $[Cu(acacP)]_2$ precursor deserves comment. It is noteworthy that the acacP ligands rearrange in the course of the oxidative addition so as to provide different ligand environments for the two electronically dissimilar metal centers (Scheme I). *The redistribution of the donor sets serves to localize the oxidation states and inhibits further oxidative addition by stabilizing the mixed-valence configuration.*[12] This rearrangement pathway is not available for symmetrical binucleating ligands.

This work has provided the first example of an odd-electron oxidative-addition process involving a bimetallic complex. Related reactivity patterns can be expected to prevail for other multimetallic assemblies when the chemistry of the constituent metals is known to deviate from the 18e rule.

Acknowledgment. This research was supported by Dow Chemical Co.

Note Added in Proof. The structure of $[Cu_2(acacP)_2(CH_3OC_6H_3CO_2)]$ is related in a number of ways to that of $PtCl_2[Cu(acacP)_2]$. See: Wrobleski, D. A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 2314.

Supplementary Material Available: Listings of positional and thermal parameters and structure factors (26 pages). Ordering information is given on any current masthead page.

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(5) Anal. Calcd for $C_{57}H_{53}Cu_2O_6P_2$: C, 66.92; H, 5.19; Cu, 11.06; P, 6.07. Found: C, 66.57; H, 5.24; Cu, 12.37; P, 6.09. Osmometric molecular weight (CH_2Cl_2 solution): calculated, 1022; found, 1009. ESR (frozen CH_2Cl_2 solution, −196 °C): $g_{\parallel} = 2.28$, $A_{\parallel} = 1.76 \times 10^{-2}$ cm^{-1}. UV–vis (CH_2Cl_2 (solution): λ 668 nm (ϵ 56 cm^{-1} M^{-1}), 316 nm (2.4×10^4 cm^{-1} M^{-1}), 267 nm (2.9×10^4 cm^{-1} M^{-1}). IR (mull): 1580 (s), 1555 (s), 1508 (m), 1410 (s), cm^{-1}. Magnetic moment (using Evans' method with 5% Me_4Si in $CHCl_3$): $\mu_{\text{eff}} = 1.96\ \mu_B$ (uncorrected).

(6) Jardine, F. H.; Rule, L.; Vohra, A. G. *J. Chem. Soc. A* **1970**, 238.

(7) Crystals were grown by slow (weeks) evaporation of CH_2Cl_2–methanol solutions of $[Cu_2(acacP)_2(3\text{-}ClC_6H_4CO_2)]$.

(8) Single crystals of $Cu_2(acacP)_2(3\text{-}CH_3OC_6H_4CO_2)$ are triclinic, space group $P\bar{1}\text{-}C_i^1$ (No. 2), with $a = 13.346$ (3) Å, $b = 21.308$ (5) Å, $c = 9.312$ (2) Å, $\alpha = 91.44$ (2)°, $\beta = 91.02°$, $\gamma = 81.44$ (2)°, $V = 2617$ (1) Å^3, and $Z = 2$. Three-dimensional X-ray diffraction data were collected for 12 101 independent reflections having $3.5 \leq 2\theta \leq 55.0$ on a Syntex $P2_1$ autodiffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å).

(9) The positions of the carbon atoms were constrained so that the phenyl rings maintained bond lengths of 1.395 Å and angles of 120° during refinement.

(10) The function minimized was $\sum w||F_o| - |F_c||^2$, with $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

(11) Glick, M. D.; Lintvedt, R. L. *Prog. Inorg. Chem.* **1976**, *21*, 233.

(12) Beddoes, R. L.; Connor, J. A.; Dubowski, D.; Jones, A. C.; Mills, O. S.; Price, R. *J. Chem. Soc., Dalton Trans.* **1981**, 2119.

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