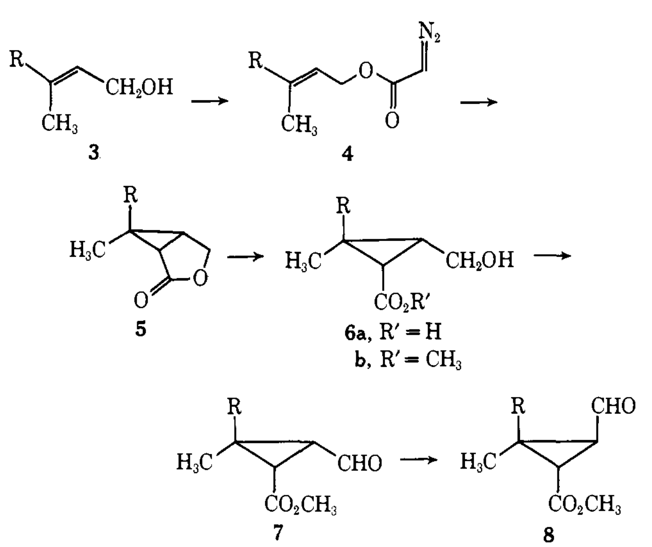
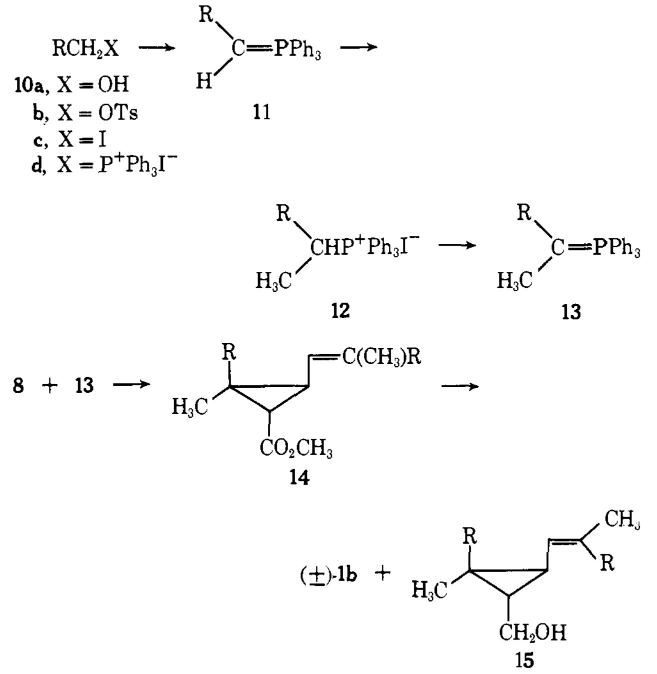


3 4

5 6a, R′ = H
b, R′ = CH₃

7 8

Phosphorane **13**, required for attachment of the second side chain, was prepared from geranylacetic acid (**9**)[14] as follows. Successive reactions with lithium aluminum hydride,[14a] tosyl chloride, sodium iodide–acetone, and triphenylphosphine in benzene gave the primary phosphonium iodide **10d** (mp 92–93°, 34% overall).[8a,b] Deprotonation with *n*-butyllithium in ether and subsequent methylation of the monosubstituted ylide **11** with a large excess of methyl iodide produced the secondary phosphonium iodide **12**;[15] addition of a second equivalent of *n*-butyllithium to **12** (after removal of the excess methyl iodide) in tetrahydrofuran furnished the disubstituted ylide **13**.



10a, X = OH
b, X = OTs
c, X = I
d, X = P⁺Ph₃I⁻

11

12 13

14

15

The Wittig reaction between the transaldehyde ester **8** and phosphorane **13** in tetrahydrofuran provided a mixture of esters **14** (57%)[8a,c] isomeric about the newly formed double bond. Reduction with lithium aluminum hydride yielded the corresponding alcohols (67%)[8c] which were separated by preparative tlc on silica gel impregnated with 7% silver nitrate.[16] The more polar and major ($\sim$2/3) isomer gave the following spectral data:[16] $\delta_{220}^{\mathrm{CDCl_3}}$ 5.12 (4 H, m), 4.94 (1 H, d, $J \sim 8$ Hz), 3.82 (1 H, 2 d, $J \sim 6$, 10 Hz), 3.56 (1 H, 2 d, $J \sim 9$, 10 Hz), 1.9–2.2 (14 H, m), 1.70 (3×3 H, s), 1.62 (4×3 H, s), 1.3–1.5 (m), 1.16 (3 H, s), 0.8–1.0 (m); *m/e* 426 (m$^+$), 408, 395, 357, 339, 289, 273, 271. The less polar isomer had very similar properties. The data are in good accord with those reported for presqualene alcohol.[3]

Radioactive samples of the two C-30 alcohol isomers, prepared by reduction of **14** with lithium aluminum tritide, were compared directly with presqualene alcohol by Professor Rilling at the University of Utah. The tlc and glc mobilities of the synthetic and natural materials were found to be essentially identical. While the pyrophosphate of the minor isomer **15** was essentially devoid of enzymatic activity, the derivative of the major isomer (±)-**1b** was converted into squalene in 33% yield (66% if only one enantiomer is active). This synthesis, therefore, confirms the structure of presqualene alcohol proposed by Rilling and Epstein[3] and establishes the relative cyclopropane stereochemistry depicted in **1b**.[17]

Acknowledgments. We are very grateful to Professor Rilling for performing the comparisons, phosphorylations, and enzymatic assays and to H. D. Pigott for the purification of **3**. Financial support from the National Institutes of Health, Eli Lilly and Company, and E. I. du Pont and Company is appreciated. Funds contributing to the purchase of the HA 220 nmr spectrometer were provided by the National Science Foundation.

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(13a) Note Added in Proof. Equilibration in methanol-*O-d* has been found to occur with incorporation of one deuterium atom (90%) adjacent to the formyl group (nmr,-CHO, s).

(14) (a) I. N. Nazarov, S. M. Makin, O. A. Shavrgin, and V. A. Smirnyagin, *Zh. Obshch. Khim.*, 30, 443 (1960); *J. Gen. Chem. USSR*, 30, 467 (1960). (b) The acid was purified *via* the *S*-benzylisothiouronium salt: D. W. Dicker and M. C. Whiting, *J. Chem. Soc.*, 1994 (1958).

(15) *Cf.* C. T. Eyles and S. Trippett, *ibid.*, *C*, 67 (1966).

(16) Although ostensibly homogeneous on tlc and glc (as TMS derivative, 3% SE-30, 240°), small extraneous absorptions can be discerned in the nmr spectra [δ 4.33 (t, J = 7 Hz), and excessive integration in the regions δ 1.3–1.5 and 0.8–1.0] and ir spectra ($\nu_{\max}$ 1730 cm^{-1}).

(17) Since the reaction between **8** and **14** is evidently the first synthesis of a trisubstituted olefin with an unsymmetrical dialkylphosphorane, the geometry about the double bond cannot be assigned with certainty at this time.

Chemistry of the Copper–Dithiooxalate Complexes. The Synthesis of a New Carbonyl Sulfide Complex

Sir:

Dithiooxalato complexes in which the dithiooxalate ligands are sulfur bonded to the central metal ions interact with coordinatively unsaturated metal complexes, giving rise to polynuclear coordination compounds. These interactions, which stem from the ability of the carbonyl groups to function as donors for Lewis acids, are manifested in the electronic and structural characteristics of the ternary complexes.[1,2] A study of the chemistry of the bis(dithiooxalato)copper-

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(1) D. Coucouvanis, *J. Amer. Chem. Soc.*, **92**, 707 (1970).

(2) D. Coucouvanis, R. E. Coffman, and D. Piltingsrud, *ibid.*, **92**, 5004 (1970).

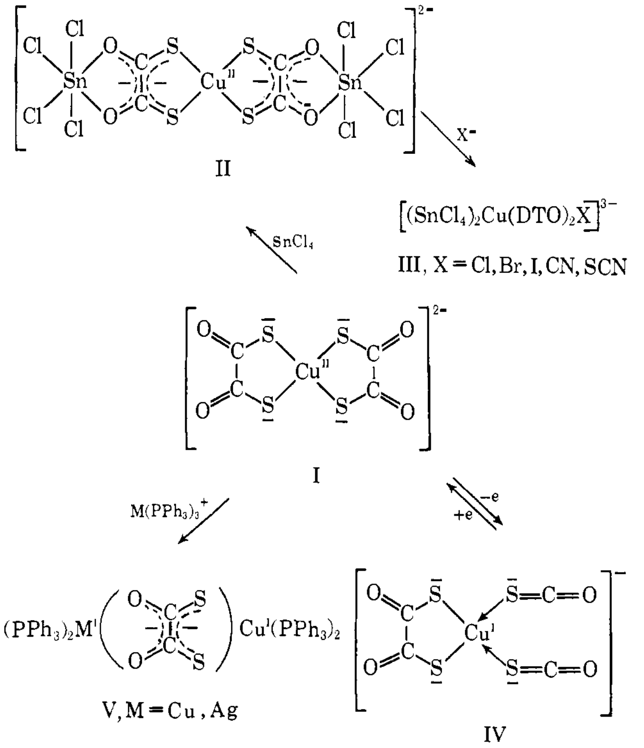
Table I. Physical Properties of the Copper–Dithiooxalate Complexes

Complex	Mp, °C	% C, calcd (found)	% H, calcd (found)	% Cu, calcd (found)	$\nu_{C=O}$, cm^{-1}	μ_{eff}^{cor}, BM[d]	E_p[e,f]
I, $(BzPh_3P)_2Cu(Dto)_2$	169–170	64.20 (64.38)	4.36 (4.37)	6.29 (6.25)	1620 (s)[a,b] 1585 (s)	1.81 ± 0.05	+0.27 ± 0.03[g]
II, $[(PPh_3)_2N]_2Cu(Dto)_2(SnCl_4)_2$[j]	160–162	48.00 (47.45)	3.16 (3.06)	3.34 (3.16)	1475 (s)[a,b]	1.83 ± 0.05	
III, $(Ph_4As)_3Cu(Dto)_2(SnCl_4)_2Cl$	161–162	45.35 (44.74)	2.98 (3.20)	3.16 (3.08)	1365 (s)[a,b]	Diamagnetic	
IV, $(Ph_4As)Cu(Dto)(SCO)_2$	[l]	48.9 (49.03)	2.92 (2.66)	9.25 (9.39)	2035 (s)[a,b] 1642 (s) 1592 (s)	Diamagnetic	−0.24 ± 0.03[h]
$(BzPh_3P)Cu(Dto)$-$(SCO)_2 \cdot CH_2Cl_2$[k]		48.55 (48.83)	3.24 (3.26)	8.56 (8.31)	2031 (s)[a,b] 1640 (s) 1590 (s)	Diamagnetic	−0.25 ± 0.03[h]
V, $(PPh_3)_2Cu(Dto)Cu(PPh_3)_2$	205–207	68.6 (68.17)	4.64 (4.58)		1528 (s)[c]	Diamagnetic	
$(PPh_3)_2Ag(Dto)Ag(PPh_3)_2$[i]	168–170	64.51 (63.80)	4.34 (4.54)		1545 (s)[c]	Diamagnetic	

[a] Nujol mull between NaCl plates. [b] CH_2Cl_2 solution. [c] KBr disk. [d] Determined by a Faraday technique. [e] Cyclic voltammetry in CH_2Cl_2 *vs.* Ag|AgI; *n*-Bu_4NClO_4 was used as the supporting electrolyte. [f] Values at a scan rate of 0.2 V/sec. [g] Oxidation wave. [h] Reduction wave. [i] Silver analysis: calcd, 15.51; found, 15.52. [j] Nitrogen analysis: calcd, 1.48; found, 1.60. [k] The presence of CH_2Cl_2 was verified in the mass spectrum of this compound. [l] Evolution of COS occurs at 120°.

(II) complex, $Cu(Dto)_2^{2-}$ (I), has produced new results attributable to the properties of the dithiooxalate ligand. Perhaps the most interesting of these results is *the oxidative cleavage of the carbon–carbon bond in the coordinated ligand which gives rise to a new, sulfur-bonded, carbonyl sulfide complex.* In this note we present a preliminary account of our studies, which are summarized in Table I and Scheme I.

Scheme I



The tetraphenylarsonium, Ph_4As^+, salt of I precipitates from an aqueous solution of $K_2Cu(Dto)_2$[3] upon the addition of aqueous Ph_4AsCl. The crude precipitate can be recrystallized from a 1:4 dimethylformamide–ether mixture.[4] The crystalline $(Ph_4As)_2$-$Cu(Dto)_2$ is X-ray isomorphous to the corresponding Ni(II) and Pd(II) planar complexes,[6] suggesting a planar structure[7] for I. In a manner analogous to the one reported for the nickel(II)- and palladium(II)-dithiooxalato complexes,[1] $SnCl_4$ reacts with I in a 2:1 molar ratio to afford $[Cu(Dto)_2(SnCl_4)_2]^{2-}$ (II).

Thus, when the bis(triphenylphosphine)iminium, $(PPh_3)_2N^+$, salt of I[4] in CH_2Cl_2 solution is treated with a CH_2Cl_2 solution of anhydrous $SnCl_4$ and the ensuing green solution is diluted with *n*-pentane, crystals of $[(PPh_3)_2N]_2[Cu(Dto)_2(SnCl_4)_2]$ are obtained. The physical properties of this compound (Table I), and particularly the low frequency of the C–O stretching vibration, suggest a structure for II similar to the one proposed[1] for the analogous Ni(II) and Pd(II) complexes (Scheme I).

Upon the addition of polar solvents (*i.e.*, DMF, CH_3CN, H_2O) or nucleophiles (*i.e.*, Cl^-, Br^-, I^-, CN^-, SCN^-, etc.), CH_2Cl_2 solutions of II change color from green to deep violet. Continuous-variation plots[9] for the systems II–Cl, II–I, and II–CN revealed the formation of 1:1 adducts of the type $[Cu(dto)_2(SnCl_4)_2X]^{3-}$ (III, X = Cl^-, I^-, or CN^-). The crystalline Ph_4As^+ salt of III (X = Cl) was obtained by the reaction between the Ph_4As^+ salt of I, anhydrous $SnCl_4$, and Ph_4AsCl in CH_2Cl_2 in a 1:2:1 molar ratio. The violet oil, which resulted when an excess of *n*-pentane was added to the solution, was redissolved in CH_2Cl_2 and crystallized by the addition of $CHCl_3$. The physical properties of this compound (Table I), and in par-

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(3) R. G. Pearson and D. A. Sweigart, *Inorg. Chem.*, 9, 1167 (1970).

(4) Benzyltriphenylphosphonium ($BzPh_3P^+$) and the bis(triphenylphosphine)iminium,[5] $(PPh_3)_2N^+$, salts of I were prepared by a similar synthetic procedure.

(5) J. K. Ruff and W. N. Schlientz, Department of Chemistry, University of Georgia, private communication.

(6) E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 1475 (1935).

(7) The magnetic moment of the Ph_4As^+ salt of I (1.81 BM at 300°K) and epr spectra compare favorably with similar measurements reported for other planar Cu(II)–sulfur complexes.[8]

(8) D. Coucouvanis, *Progr. Inorg. Chem.*, 11, 233 (1970).

(9) These studies were performed spectrophotometrically in CH_2Cl_2 with $[(Ph_3P)_2N]_2[Cu(Dto)_2(SnCl_4)_2]$ and the corresponding $(Ph_3P)_2N^+$ salts of Cl^-, I^-, and CN^-.

ticular its diamagnetic character, suggest a structure in which either Cu–Cu interactions or antiferromagnetic coupling of spins results in a singlet ground state. The molecular weight of this complex, determined osmometrically in 0.02 *M* acetone and 1,2-dichloroethane solutions, was 1257 ± 20 and 2220 ± 40, respectively. Assuming complete ionic association, molecular weights of 2009 and 4018 are calculated for the monomer and dimer, respectively. The observed values can tentatively be ascribed to a dimeric hexaanion which shows different degrees of ionic associations depending on the dielectric constants of the solvents employed. The exact nature of III is still uncertain, however, and a complete description of its structure must await the results of further studies now in progress.

Attempts were made to replace the inert counterion of I with $(PPh_3)_2M^+$ [M = Cu(I) or Ag(I)]. The products obtained when aqueous solutions of I were extracted with CH_2Cl_2 solutions of $(PPh_3)_3MCl$ had the stoichiometry $(PPh_3)_2Cu^I(Dto)M(PPh_3)_2$ [M = Cu(I) or Ag(I)]. The same compounds as well as $(PPh_3)_2AgDtoAg(PPh_3)_2$ could also be obtained from K_2Dto and $M(PPh_3)_3Cl$ by a similar extraction procedure. The mode of coordination of the (presumed bridging) dithiooxalate ligand in these diamagnetic, X-ray-isomorphous complexes is at present uncertain.

Cyclic voltammetry on solutions of the Ph_4As^+ salts of I in CH_2Cl_2 (Table I) revealed the existence of a reversible one-electron oxidation at scan speeds $\leqslant 0.1$ V/sec. At scan speeds >0.2 V/sec a quasi-reversible wave[10] was observed, as evidenced by the separation between the anodic and cathodic portions of the wave ($E_p > 60$ mV). Chemical oxidation of solutions of the Ph_4As^+ or $BzPh_3P^+$ salts of I in DMF or CH_2Cl_2 by $CuCl_2 \cdot 2H_2O$ or anhydrous $FeCl_3$, respectively, gave rise to red, diamagnetic crystalline compounds of the composition $CatCu(Dto)_2$ (IV) (Cat = Ph_4As^+ or $BzPh_3P^+$). The infrared spectra of these light-sensitive compounds revealed the presence of coordinated dithiooxalate ligand[1] (Table I) and a new strong band at 2035 cm^{-1}. Addition of PPh_3 to dichloromethane solutions of IV led to a vigorous evolution of gas. The infrared and mass specta of this gas were found to be identical with those of gaseous COS.[11] The high C–O stretching frequencies observed at 2035 cm^{-1} in the ir spectra of IV suggest that the OCS molecule is coordinate "end-on" *via* the sulfur end of the molecule.[12] The electrochemical behavior of IV was examined by cyclic voltammetry and it was found that IV undergoes a reversible one-electron *reduction* at scan rates $\leqslant 0.1$ V/sec. At rates >0.2 V/sec a quasi-reversible wave was obtained. The potential at which IV undergoes reduction is approximately equal, and of opposite sign, to the potential at which oxidation of I is observed (Table I). Chemical reduction of IV in tetrahydrofuran (THF) with $NaBH_4$ occurs readily, and the major product isolated was the "parent" copper dithiooxalate. The electrochemical properties of I and IV (Table I) suggest[14] that the electron-transfer rate in either the reduction of IV or the oxidation of I is slow, consistent with a redox scheme involving the breaking and forming of a C–C bond.[15]

$$[\mathrm{Cu^{II}(Dto)_2}]^{2-} \underset{+e}{\overset{-e}{\rightleftharpoons}} [\mathrm{Cu^{I}(COS)_2Dto}]^- \tag{1}$$

As a final comment, we would like to suggest that oxidation of the coordinated dithiooxalate ligand may provide a convenient general synthetic route to carbonyl sulfide complexes.

Acknowledgment. This study was supported in part by Grant No. PRF 1775-G3 from the Petroleum Research Fund, administered by the American Chemical Society

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[10] R. S. Nicholson, *Anal. Chem.*, 37, 1351 (1965).

[11] The C–O stretching vibration in gaseous COS is found at 2064 cm^{-1}.

[12] A similar type of "end-on" coordination has been reported[13] to occur in a carbon disulfide complex of rhodium ($RhCl(CS_2)_2(PPh_3)_2$). The terminal C=S stretching frequency in this compound is found at 1510 cm^{-1}, and is 20 cm^{-1} smaller than the corresponding vibrational frequency in gaseous CS_2. The C–O stretch in COS which is σ bonded to platinum *via* carbon and sulfur atoms occurs at 1727 cm^{-1}.[13]

[13] M. C. Baird and G. Wilkinson, *J. Chem. Soc.*, 865 (1967).

[14] The mechanism of these redox processes is currently being investigated.

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Intramolecular Redox Equilibria of Cobalt–Nitrosyl Complexes

Sir:

The controversial nature of the nitrosyl ligand has been somewhat clarified by recent precise X-ray diffraction studies which in most cases illustrate either of two distinct NO bonding modes.[1] In the sense of formal oxidation states, this ligand behaves as ^+NO in some complexes and as ^-NO in others.[2] The former are characterized by linear metal–N–O bonds and rather short metal–N distances, whereas the latter exhibit metal–N–O angles approaching 120° and longer metal–N distances. Recently, we suggested[3] the possibility of conformational equilibria between the two forms of metal–nitrosyl bonding whereby the coordination geometry about the metal would change as the metal and the nitrosyl undergo a formal internal redox reaction. Experimental evidence consistent with such hybridization isomerism is presented below.

The most dramatic example of the dual nature of NO ligands is Eisenberg's report[4] of **1** wherein the two nitrosyl groups are found in the two limiting bonding modes. We have repeated the synthesis of **1** using isotopically labeled $RuCl(^{15}NO)(P(C_6H_5)_3)_2$ (**2**). During the 15 min required for isolation from methanol, four NO bands appear (Table I), indicating equilibration of the two forms in solution.

This interconversion is a restricted example of the hybridization tautomerism we had suggested earlier in that the two equilibrating forms are identical and

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[1] (a) B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, 8, 1288 (1969); (b) J. H. Enemark and J. A. Ibers, *ibid.*, 7, 2339 (1968); (c) D. J. Hodgson and J. A. Ibers, *ibid.*, 7, 2345 (1968); (d) *ibid.*, 8, 1282 (1969).

[2] The use of the terms ^+NO and ^-NO is not intended to reflect the probable electron densities on the NO ligands in these complexes but rather to assign formal oxidation numbers to the central element.

[3] J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, 91, 5659 (1969).

[4] C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *ibid.*, 92, 4760 (1970).