

The assignment ventured in Table I is necessarily different from those suggested by McGlynn, *et al.*,¹ and Diemann and Müller,⁴ though we would infer the same sequence of orbital ionization as the latter workers, namely $1t_1 < 3t_2 < 1e < 2a_1 < 2t_2$. In the case of OsO_4 , we differ from McGlynn and coworkers only with regard to the assignment of the first two PE bands. The identification of the first band with the 2T_2 ($3t_2^{-1}$) ion state was based on a detailed analysis of its vibrational fine structure and, in particular, on the discovery of a vibronic splitting of some 50 cm^{-1} in the secondary vibrational progression associated with the ν_2 (e) mode. Yet it is by no means inconceivable that such fine structure might arise for the t_1 ionizations, despite the non-bonding character of the t_1 orbitals. We recall that a vibronic splitting of almost 0.1 eV ($\sim 800\text{ cm}^{-1}$) is observed in the 2T_1 (t_1^{-1}) band of CBr_4 . We prefer to associate the first band in both the OsO_4 and RuO_4 spectra with the 2T_1 ion state, an assignment based in part on analogy with the case history for TiCl_4 and TiBr_4 (also d^0 molecules),⁵ and in part on the currently accepted sequence of one-electron energy levels deduced from the electronic absorption spectra of both tetroxo (MO_4)⁶ and tetrahalo (MX_4)⁷ d^0 species. Moreover, the sequence of orbital energies, $1t_1 > 3t_2$, implied by the assignments in Table I, is in agreement with the results of *ab initio* LCAO-MO SCF calculations on species such as MnO_4^- ⁸ (though we must of course recognize that differential relaxation effects may invalidate the qualitative trends expected from Koopmans' theorem).

The interpretation of their RuO_4 spectrum favored by McGlynn and coworkers is naturally much confused by the impurity band. The same may be said of the discussion by Diemann and Müller of both their OsO_4 and RuO_4 spectra. Actually, the latter workers argue for the assignment of bands B and C in the OsO_4 spectrum to split components of the 2T_2 ($3t_2^{-1}$) ion state. This would be barely conceivable unless the perturbing agency involved were spin-orbit coupling centered about the osmium atom, and this possibility may be ruled out simply on the grounds that the sequence of ion multiplet states, E'' (2T_2) $>$ U' (2T_2), indicated by the relative intensities of bands B and C, is qualitatively incorrect for the $t_2(d)^5$ configuration.^{5,9}

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Preparation and Characterization of Copper(I) and Silver(I) Complexes of *O*-Ethylboranocarbonate

Sir:

The isoelectronic analogy between borane (BH_3) and oxygen has been developed in detail for several systems including the carbonate (CO_3^{2-})-boranocarbonate (H_3BCO_2^-) system and the *O*-ethylcarbonate (CO_2^-)

OC_2H_5^-)-*O*-ethylboranocarbonate ($\text{H}_3\text{BCO}_2\text{C}_2\text{H}_5^-$) system.^{1,2} Although suggestion of the coordination of the boranocarbonate species to transition metals has been made, no isolation or characterization of such complexes has been reported.^{3,4} We wish to report the first metal complexes of the *O*-ethylboranocarbonate anion: *O*-ethylboranocarbonatobis(triphenylphosphine)copper(I), $(\text{Ph}_3\text{P})_2\text{CuH}_3\text{BCOOC}_2\text{H}_5$, and *O*-ethylboranocarbonatotris(triphenylphosphine)silver(I), $(\text{Ph}_3\text{P})_3\text{AgH}_3\text{BCOOC}_2\text{H}_5$. The compounds result from the reaction of $(\text{Ph}_3\text{P})_3\text{CuCl}$ or $(\text{Ph}_3\text{P})_3\text{AgNO}_3$ and $\text{KH}_3\text{BCOOC}_2\text{H}_5$ in CHCl_3 and ethanol using an excess of triphenylphosphine. The compounds have been identified using elemental analysis, molecular weight data, and ir and nmr spectral data.

Elemental analysis support the formulations given. *Anal.* Calcd for $(\text{Ph}_3\text{P})_2\text{CuH}_3\text{BCOOC}_2\text{H}_5$: C, 69.42; H, 5.64; P, 9.18. Found: C, 69.66; H, 5.66; P, 9.16. Calcd for $(\text{Ph}_3\text{P})_3\text{AgH}_3\text{BCOOC}_2\text{H}_5$: C, 69.74; H, 5.44; P, 9.47; Ag, 10.98. Found: C, 69.75; H, 5.54; P, 9.66; Ag, 9.95. Molecular weights in CHCl_3 by vapor pressure osmometry resulted in the following values: $(\text{Ph}_3\text{P})_2\text{CuH}_3\text{BCOOC}_2\text{H}_5$ (0.0504 *M*) exptl 574, calcd 674.7; $(\text{Ph}_3\text{P})_3\text{AgH}_3\text{BCOOC}_2\text{H}_5$ (0.0428 + 0.0382 *M* Ph_3P) exptl 501, calcd 981.7. The deviation of the experimental value from the calculated value is typical of complexes of this type and is attributed to the complex equilibria present due to dissociation by the phosphine when the compounds are dissolved in organic solvents.^{5,6} Addition of the excess triphenylphosphine was necessary in the case of the silver complex to allow measurements to be carried out with a minimum of decomposition which is evidenced by the formation of metallic silver. Addition of triphenylphosphine to solutions of the copper and silver compounds increased the values for the molecular weights which is consistent with a depression of the dissociation by the phosphine ligands.

The infrared spectra of the copper and silver complexes in CHCl_3 consist of the following absorption bands (only absorptions which directly pertain to the proposed structures are included): $(\text{Ph}_3\text{P})_2\text{CuH}_3\text{BCOOC}_2\text{H}_5$ (absorption (cm^{-1}), relative intensity, tentative assignment), 2990 (m) $\nu_{\text{CH}_3(\text{asym})}$, 2970 (m) $\nu_{\text{CH}_2(\text{asym})}$, 2940 (sh) $\nu_{\text{CH}_3(\text{sym})}$, 2900 (w) $\nu_{\text{CH}_2(\text{sym})}$, 2380 (m) $\nu_{\text{terminal B-H}}$, 1655 (vs) $\nu_{\text{C=O}}$; $(\text{Ph}_3\text{P})_3\text{AgH}_3\text{BCOOC}_2\text{H}_5$ 2980 (m) $\nu_{\text{CH}_3(\text{asym})}$, 2960 (sh, w) $\nu_{\text{CH}_2(\text{asym})}$, 2940 (w) $\nu_{\text{CH}_3(\text{sym})}$, 2900 (w) $\nu_{\text{CH}_2(\text{sym})}$, 2330, 2270 (m) $\nu_{\text{terminal B-H}}$, 2080 (m) $\nu_{\text{bridge B-H}}$, 1640 (vs) $\nu_{\text{C=O}}$.

The spectra of both complexes are characteristic of coordination *via* the hydrogens in the borane group since terminal B-H stretching absorptions near 2400 cm^{-1} as well as bridging M-H-B absorptions near 2000 cm^{-1} are observed. Moreover, the absorption near 1630 cm^{-1} characteristic of the carbonyl stretching mode of the ethylboranocarbonate anion appears to undergo little change upon complexation. The positions of the B-H absorption bands in the copper as compared to

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the silver complex suggest a greater degree of ionic bonding in the latter since the terminal B-H absorptions are at lower frequency in the silver and the bridging B-H absorptions are much higher.⁷ Both *O*-ethylboranocarbonate complexes appear to be more ionic than the corresponding BH₄⁻ complexes on the same basis. The doublet in the silver complex along with the resultant peak separation of approximately 60 cm⁻¹ indicate the presence of two terminal hydrogens;⁷ the peaks correspond to the asymmetric and the symmetric stretching modes. This assignment requires then, that the Ag-H-B complex bonding system consists of a single bridging hydrogen as compared to two bridging hydrogens in the copper complex (the analogous double bridged system is also found in the copper BH₄⁻ complex).⁸ This monodentate structure, though not established thus far for metal complexes, is analogous to the single-hydrogen-bridged structure proposed for B₂H₇⁻⁹ and (R₃B)₂H⁻^{9a,10} compounds.

The ¹¹B nmr spectra of the copper and silver complexes in CDCl₃ are identical in band shape; both consist of a broad quartet of approximate ratio 1:3:3:1 (ambient temperature, δ_{Ag complex} 33.3 ppm from BF₃OEt₂, J_{BH} = 80 Hz; δ_{Cu complex} 25.2 ppm from BF₃OEt₂, J_{BH} = 70 Hz). Although the quartet may be rationalized by splitting of the boron signal by the two different types of hydrogen attached to the boron (one terminal and two bridged or two terminal and one bridged), the best explanation perhaps is that the splitting of the boron signal and the resultant broadened peaks occur due to the presence of three equivalent hydrogens which are equivalent by virtue of an intramolecular bridge-terminal exchange process.¹¹ This explanation is not in conflict with the ir data since vibrational spectroscopy, with a faster time scale, can provide useful structural data in contrast to nmr spectroscopy which provides, in this case, useful electronic information.⁷ Broadening of the peaks could be due to a spin-lattice relaxation effect.^{11b,c} Such a "thermal decoupling" effect would be clarified by variable temperature studies, the results of which will be reported in a later paper. The difference in chemical shift values supports the difference in the singly and doubly bridged structures on an inductive basis, with the exchanging hydrogens occupying one or two coordination sites, respectively.

The ¹H nmr spectrum (ambient temperature, CDCl₃) confirms the presence of the ethyl group in the complexes (all shifts are downfield from TMS): M = Ag; δ_{CH₂} 3.84 ppm, J_{CH₂} = 7 Hz; δ_{CH₃} 0.94, J_{CH₃} = 7 Hz; M = Cu, δ_{CH₂} 3.58, J_{CH₂} = 7 Hz, δ_{CH₃} 0.89, J_{CH₃} = 7 Hz. The lack of observation of the B-H protons in the ¹H nmr supports coordination by the hydrogens of the borane group since the ethylboranocarbonate anion itself shows a fairly sharp 1:1:1:1 quartet (ambient temperature, CD₃OD, δ 0.77 ppm downfield to TMS,

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J_{BH} = 83 Hz). Thus, upon coordination the symmetry at the boron is changed such that the effect of extensive ¹⁰B and ¹¹B coupling to hydrogen in addition to an exchange process alluded to in the discussion of the boron nmr spectra results in the nondetection of the B-H proton absorptions.

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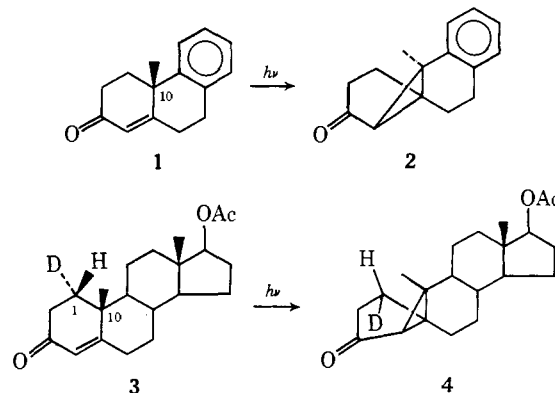
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Absolute Stereochemistry of Photorearrangement of a Simple Chiral 4,4-Dialkylcyclohexenone¹

Sir:

The photochemical rearrangements of substituted 2-cyclohexenones continue to fascinate chemists.² Not the least of the problems which remains unresolved is the source of the extremely high inefficiency (~99%) on photoexcitation of such compounds.² Substituents on the olefinic moiety often wipe out reactivity altogether.³ We have been engaged in studies to explore the possibilities of reversible biradical formation as the source of energy wastage in these systems, using stereochemistry and kinetics as experimental probes.⁴

Prior stereochemical studies have been confined to polycyclic enones. Thus, Chapman, *et al.*, demonstrated that the photorearrangement of **1** to **2** proceeded with ≥95% retention of optical activity,⁵ while Schaffner and coworkers⁶ showed that the configuration at C₁ in **3** was retained on photorearrangement to **4**. Be-



cause of the necessary *cis* fusion of the cyclopropane to the five- and six-membered rings in **2** and **4**, the lumiketone rearrangement in both these systems^{5,6} must proceed with inversion of configuration at C₁₀. While

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